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THE COMPRESSIBILITY OF THIRTY METALS AS A FUNCTION OF PRESSURE AND TEMPERATURE.

BY P. W. BRIDGMAN.

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(Continued from page 3 of cover.)

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Introduction.

Our present knowledge of the compressibility of metals is mostly due to the work of Richards [1] and his collaborators, and to Adams Williamson and Johnston.[2] (I shall abbreviate reference to these authors by A. W. J.) Richards has measured the compressibility of a large number of metals over a pressure range of 500 kg. at room temperature. A. W. J. have measured the compressibility of a smaller number of metals over the much wider pressure range of 10000 kg/cm^2, but again only at room temperature. The work of Richards, therefore, does not enable us to find either the pressure or the temperature variation of compressibility, and although the work of A. W. J. gives valuable information as to the variation of compressibility with pressure, they have themselves recognized that the pressure variations so found are not accurate.

Recent theoretical work, in particular that of Born[3] is now bringing within the reach of the possibility of computation the compressibility of substances in terms of their crystalline structure. Born's theory of the compressibility of substances of the type of sodium chloride is far enough advanced to give an expression for the variation of compressibility with pressure. It seems therefore that the time is ripe for a more careful experimental examination of the question of the compressibility of the metals, although we may not have as yet a satisfactory theory of the metallic state itself.

The experimental work of this paper consists of a determination of the compressibility of 30 metals over a pressure range of 12000 kg/cm^2 at 30° and 75°. This range is sufficient to give the pressure and temperature coefficients of the compressibility.

The question of experimental accuracy is an important one here. It is well known that compressibility is one of the harder quantities to measure experimentally, so that all the more is it difficult to measure the pressure or the temperature coefficient of compressibility. The use of high pressure is indispensable here, for by increasing the magnitude of the effects to be measured it is possible to attain the necessary accuracy. This is particularly true with respect to the pressure coefficient of compressibility; the accuracy with which this may be determined increases as the square of the pressure range. Other things being equal, therefore, it should be possible with the pressure range of this work to determine the pressure coefficient 576 times as accurately as possible over a pressure range of 500 kg.

A new method of measuring compressibility has been developed for this work, which has very considerable advantages, both of speed and accuracy, over previous methods. As compared with previous methods, the accuracy of this is much increased by the fact that all the corrections are very much less. The method essentially involves the measurement of the difference of linear compressibility between the substance in question and pure iron. If the absolute linear compressibility of iron is known, we have at once the linear compressibility of the substance in a definite direction, and if equal compressibility in all directions is assumed, the true volume compressibility may be computed. It is to be noticed that over the pressure range used here, the compressibility cannot be found by simple multiplication by the factor three, but a correction has to be applied, which in some cases may rise to the order of ten per cent.

The assumption that the substance is equally compressible in all directions is applicable only when the material is amorphous or when it belongs to that one of the crystalline systems enjoying this property, namely the cubic. This assumption is true for the majority of metals, but it is definitely not true for several, which may have very materially different compressibilities in different directions. For these substances it is necessary to measure the linear compressibility in several directions in order to get the true cubic compressibility. This is at once a disadvantage and an advantage; the determination of the average cubic compressibility becomes more complicated than by the methods employed by Richards or A. W. J., but on the other hand the average cubic compressibility is not a datum of much significance in these cases, whereas it is possible by the use of the present method to obtain a complete description of the behavior under pressure. For substances of this type it is necessary to have single crystals. The growth of such crystals involves a technique in itself; in this paper only the beginnings of the attack on this subject are made. I have shown for a number of non-cubic crystals that there may be very great differences of linear compressibility in different directions, and have made a promising beginning at a method of obtaining metals with a uniform crystalline orientation throughout the entire mass. The further examination of this important question must be left for future work.

With regard even to those metals which are known to crystallize in the cubic system it is not safe to assume without some examination that the linear compressibility is the same in every direction, for few masses of metal are unicrystalline, but there are also regions of

amorphous cementing material. In a number of cases I have tried, therefore, to justify this assumption. A number of years ago I measured the compressibility of commercial iron in the form of boiler plate along and across the direction of rolling,[4] and could find no difference in the linear compressibility. I have now repeated the same examination for rolled copper, and again could find no difference. Also, in several cases I have measured the compressibility, first in the shape of the unworked casting, and then after the casting had been extruded to a considerably smaller diameter, so that the crystalline grains were much distorted by working, and presumably considerable amorphous material was introduced. The general result of this work is that no perceptible change of linear compressibility is produced in this way, and it is highly probable that the assumption is correct that the ordinary cast or worked forms of those metals that crystallize in the cubic system have the same compressibility in every direction. The correctness of this assumption may further be checked by a comparison of the results obtained by my method with those obtained by the other methods, which are essentially methods for measuring the cubic compressibility.

The absolute linear compressibility of iron has been previously measured by me at two different temperatures.[5] I did not succeed in finding any departure of the compressibility from constancy over a pressure range of 10000 kg., but I did find an increase of compressibility at the higher temperature. This early work was unsatisfactory to me for two reasons. In the first place the theoretical considerations of Born would suggest that the departure of compressibility from constancy at high pressures should be large enough to measure even for a metal as little compressible as iron, and in the second place I could not help feeling that my temperature coefficient was too high. I therefore have made a fresh experimental attack on this question, greatly improving the experimental method, and have been able to definitely find and measure with some accuracy the change of compressibility of iron with pressure, and to show that the temperature coefficient is several times smaller than previously found.

This experimental work falls into two parts; first the redetermination of the absolute linear compressibility of iron, and second the determination of the relative linear compressibility of iron and 29 other solid metals.

The Absolute Compressibility of Iron.

The method adopted is in many respects like that previously used. An iron rod approximately 30 cm. long is placed inside a heavy cylinder and exposed to hydrostatic pressure exerted by a fluid filling the cylinder. The relative change of length of the rod and the cylinder is measured, and at the same time the change of length of the cylinder is measured at outside points. From these two the absolute change of length of the iron rod under pressure may be computed. The only assumption is that the change of length of the cylinder externally, where it can be measured, is the same as that internally, where it is in contact with the rod. This assumption is entirely justified if the cylinder extends some distance beyond the end of the rod, so that warping of the cross section due to end effects is negligible, and in any event the assumption is of little importance because the correction for the change of length of the cylinder is only a few per cent of the entire effect.

The essential difference between the old and the new method is in the means of measuring the relative change of length of the rod and the cylinder. Previously the rod carried a collar which bore against a fixed shoulder in the cylinder and whose relative displacement on the rod was measured after every application of pressure. This involved a complete setting up and disassembly of the apparatus for a single reading at any pressure. The present method is a continuous reading one. Attached to the end of the rod is a fine wire of high resistance alloy. This wire slides over a contact fixed to the cylinder. The sliding contact is made one potential terminal and another potential terminal is attached to a point of the wire. Current is passed through the wire independently of the potential terminals, entering the wire at one end and leaving at the other. The difference of potential between the fixed and the sliding point on the wire is measured for a given current, so that the resistance and hence the length of the wire between terminals may be calculated, and hence the relative motion of the rod and the cylinder. The reading is continuous, and after every change of pressure a new reading may be obtained in a few minutes, or as soon as the heat of compression is dissipated. Further, there is no error from the constant possibility of introducing minute particles of dirt every time the apparatus is opened, as there was previously.

The essentials of the apparatus are shown in Figure 1. The high

resistance wire B (which is of nichrome) is mounted in a steel plunger A which is kept pressed by a spring against the upper end of the bar at S. The wire B slides over a contact at C which is attached to the plate D insulated by mica washers at E from the rest of the cylinder. At F the second potential terminal is soldered to the wire B, and at the end G is attached the current terminal. The other terminal is the cylinder itself, to which the lower end of B is grounded. The three wires from C, F, and G are attached at the upper end of the

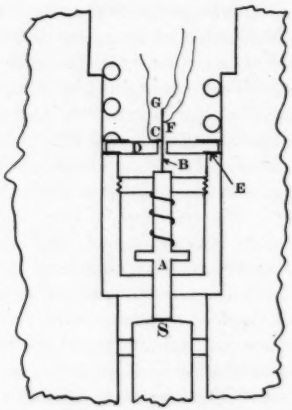

FIGURE 1. The sliding electrical contact device for measuring the absolute linear compressibility of iron.

cylinder to a three terminal plug, of exactly the same design as used in previous work on electrical resistance under pressure. The plate D is kept rigidly in position by springs shown in section, which are compressed as the three terminal plug is screwed into place. There are various mechanical details not shown in the drawing to facilitate the attaching of the connections and the general assembly. The specimen S is fixed with respect to the cylinder at the lower end. S ends in a disc which is tightly pressed against a shoulder of the cylinder by a spring (which of course must be stiffer than the spring around A) which is compressed by the connections to the pressure producing apparatus at the lower end of the cylinder.

The resistance between the points C and F was measured on the same potentiometer as was used in previous measurements of the

effect of pressure on resistance, and needs no further description. The sensitiveness of the electrical arrangements was such that a motion of the wire of 1.5×10^{-6} cm. could be detected. Of course there were always extraneous disturbances, so that an accuracy corresponding to this sensitiveness could not be obtained, but it was nevertheless possible to measure very small motions with a highly gratifying accuracy; these measurements would have been entirely impossible without some such method. This method of measuring small displacements would seem to be applicable in a number of other places.

The external change of length of the cylinder was measured somewhat differently from formerly. This was done previously with a microscope, and there were difficulties at the higher temperature (50° in the former work). The arrangement of the pressure producing part of the apparatus was such that it was now much more convenient to use the rocking mirror device familiar to many engineers. A mirror was attached to a diamond sectioned staff, which could rock between two bars, one attached to the upper end and the other to the lower end of the cylinder. The motion of the mirror was read with a telescope and scale, and the elongation of the cylinder could at once be calculated in terms of the dimensions of the various parts. The conventional devices of three point contacts and springs to ensure freedom from back-lash, etc., were used, and the apparatus functioned satisfactorily in every particular. Two measuring devices were used, attached at opposite sides of the cylinder, so that any error due to any slight Bourdon spring action of the cylinder under pressure (there usually is such action in appreciable amount) was eliminated. The method of mounting the mirrors at a distance of 30 cm. or so from the cylinder and transmitting the motion to them by bars allowed the cylinder to be placed in a temperature bath, and the temperature to be controlled by a thermostat and stirrer, as in all these experiments. The stirring of the water produced only a slight mechanical shaking of the mirrors, too slight to introduce perceptible difficulty in making the readings.

It is obvious that there are various corrections to be applied to the readings as directly obtained. The most important of these is for the effect of pressure on the resistance of the nichrome wire B. This was determined by direct experiment, and is very low; in fact this, as well as the high specific resistance, was the reason for choosing this material for the wire. The resistance between terminals fixed to the wire was found to decrease linearly with pressure, the decrease for 12000 kg/cm^2

being 0.45%. This is much less than for any of the pure metals, and is seven times less than for manganin. It is possible to find other nickel-chromium alloys that have an even smaller coefficient, but this was so small that it was not necessary to go out of the way for other material.

Other corrections, not as important as the above, are for the temperature coefficient of resistance of nichrome wire, and for the difference of compressibility between the wire and iron. Both these corrections were determined by direct experiment; the determination of the compressibility will be described later.

Although there are several corrections to be applied, it is a unique advantage of this method that the corrections are very small, and that the greater part by far of the measured effect is the final effect that is wanted. The corrections just discussed for the change of resistance of the nichrome wire, etc., did not attain as much as 2% of the measured effect, and the correction for the external change of length of the cylinder was only 1.5%. On the other hand it frequently happens that the corrections in such methods as used by Richards or A. W. J. may be two or three times as large as the final effect wanted.

It is evident that the exact uniformity of cross section of the wire B is of vital importance if the changes of resistance are to give slight departures of compressibility from linearity with pressure. To test the uniformity of the wire a special arrangement was made consisting of two knife edges a fixed distance apart, mounted to slide along the wire, which was stretched along a meter stick. A constant current was passed along the wire, and the difference of potential between the two knife edges measured on the potentiometer. The wire was exceedingly uniform. In the first length tried, the extreme variation in a length of 20 cm. was less than 1/3000. The variation in a length of a millimeter or less was of course much smaller, and was obviously far too small to introduce any appreciable error.

The iron used for the measurement of linear compressibility was cut from a bar of American ingot iron. This iron is very pure, containing only 0.03% impurity, and was considerably purer than the piece of boiler plate whose compressibility was previously measured. The resistance under pressure of a piece cut from this same material has been previously measured.[6] The dimensions of the compressibility specimen were approximately 6 mm. in diameter and 30 cm. long. It was annealed at a red heat after machining.

The containing cylinder was especially made for this experiment and was of chrome vanadium steel from the Halcomb Steel Co., sold

by them under the name of Type D. After machining it was heat treated by quenching from 930° for a few seconds in water and then finishing the quenching in oil. It was pressure seasoned before the measurements by an application of 12500 kg., and then machined to final size. No perceptible change of dimensions was produced by this preliminary treatment.

The measurements of the external change of length of the cylinder, which were made at the same time as the measurements of the change of relative length of cylinder and bar, were entirely satisfactory. The relation between pressure and elongation was linear within the limits of error, which were not more than a few per cent, and there was no perceptible hysteresis, showing that the elastic limit had not been exceeded. However, the absolute value of the elongation was abnormal in that it was only half that which would be computed from the ordinary elastic constants of steel, assuming perfect homogeneity. It is evident that the method of heat treatment must have introduced considerable internal stress.

Measurements were made at two temperatures, 30° and 75°, and at both temperatures the runs were repeated. The two runs at each temperature agreed within the limits of error. The magnitude of the effect was sufficient to give a displacement of 40 cm. on the wire of the potentiometer. The regular procedure was followed in making readings, which were at intervals of even thousands of kilograms with increasing pressure and at the odd intervals on decreasing pressure, the maximum being 12000. There was no perceptible hysteresis. At each temperature 27 readings were taken. Two of these had to be discarded, the observed points lying off a smooth curve by slightly over 1 cm. of the potentiometer wire; the average arithmetical deviation of the remaining 52 points from smooth curves was 0.6% of the maximum effect. The departure from linearity was perfectly well marked and unmistakable; at the middle of the range it amounted to 0.32%, and was sensibly the same at both temperatures. This deviation from linearity is thus twice as great as the average error of a single observation; hence it is evident that no high degree of accuracy can be claimed for the deviation from linearity (which determines at once the pressure coefficient of compressibility), and certainly one is not entitled to more than two figures in the pressure coefficient of compressibility.

With regard to the temperature coefficient of compressibility, the change with temperature was certainly established to be much smaller than had been previously found, but again in view of the smallness of

the effect no great accuracy can be claimed for the temperature coefficient itself, and in fact not more than one significant figure could be obtained here.

After applying all corrections, including one due to the cubic compressibility not being exactly three times the linear, the following formulas were found to give the change of volume produced by any pressure p, expressed in kilograms per square centimeter.

$$\text{At } 30° \qquad \frac{\Delta V}{V_0} = -10^{-7}(5.87 - 2.1 \times 10^{-5} p)\, p$$

$$\text{At } 75° \qquad \frac{\Delta V}{V_0} = -10^{-7}(5.93 - 2.1 \times 10^{-5} p)\, p.$$

The V_0 of these formulas is in each case the volume under atmospheric pressure at 30°; the difference between the atmospheric volume at 30° and 75° would produce a change of somewhat less than one unit in the last place.

The fairest comparison of these results with those previously found is to be obtained by computing from the above formulas the average compressibility to 10000 kg., since the range of the previous work was 10000 kg., and no departure was found from linearity. The above formulas give as the average to 10000, 5.66×10^{-7} at 30° and 5.72×10^{-7} at 75°. These are materially smaller than the previous values, which were 5.83×10^{-7} at 0° and 6.01×10^{-7} at 50°. Probably part of the difference is to be explained by the greater purity of the present specimen, it being consistent with a number of my other observations that alloying iron increases its compressibility, but doubtless the important part of the difference is to be ascribed simply to the improvement in the method; certainly the present determination of the temperature effect is to be preferred to the previous one.

The new value for the compressibility of iron will not affect at all the compressibilities given by Richards, which involve my previous value for iron indirectly through the value for mercury, but will lower the absolute values of compressibility given by A. W. J. by 0.25×10^{-7}, since their values also depend on my value for iron. The fact that the compressibility of iron is now found to decrease somewhat at high pressures will also of course somewhat increase the estimate of A. W. J. of the decrease of compressibility with pressure.

The instantaneous compressibility, which I define as $\frac{1}{V_0}\frac{dV}{dp}$, may be found from the above formulas by differentiation. The change of

compressibility with pressure is thus seen to be about 8.5%. One would not suspect so large a change from the slight apparent departure from linearity of the curve plotting change of length against pressure.

Compressibility of Metals Other than Iron.

METHOD.

The general idea of the method is the same as that used for the absolute linear compressibility of iron, namely a wire is attached to the specimen, which slides over a contact fixed to a comparison piece, and the relative motion of the wire is obtained from a measurement of the potential difference between the sliding contact and the contact fixed to the wire. In this case, however, the comparison piece is not the external cylinder itself, but is another piece of iron within the cylinder which is exposed to hydrostatic pressure all over, and which therefore experiences only a uniform compression. The amount of this compression is determined by the measurements on iron just described.

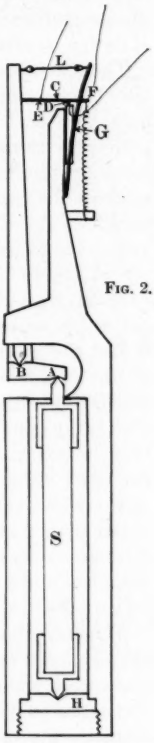

FIG. 2.

Several forms of apparatus were used, depending on the numerical value of compressibility and the shape in which the specimens could be obtained. For those substances whose compressibility is near to that of iron, an apparatus with a lever was used, by which the relative motion of the specimen and the surrounding iron was magnified about seven times. A sketch of the essential parts is shown in Figure 2. The specimen shown at S was, when convenient, made in the form of a turned bar 6 mm. in diameter. Over each end was slipped a well fitting steel cap, provided with steel points. At the lower end one of these points rested against the containing envelope of iron, and at the upper end the other point bore against the short arm of the lever. This lever had three point support, one at A, and two, one behind the other, at B. The lever was kept tightly pressed against the specimen by a spring of flat steel G,

FIGURE 2. Device with lever magnification and sliding electrical contact for measuring the difference between the linear compressibility of iron and the specimen S.

pulling on the upper end of the lever through a link motion L. The nichrome measuring wire C is attached to the upper end of the lever, and slides over a contact at D which is attached to a plate insulated from the rest of the apparatus with a thin mica washer. At E is the potential terminal fixed to the wire. Flexible leads pass from E and D to the two potential terminals of the three terminal plug, and the current terminal is attached at F. The second current connection is simply the case, to which everything is grounded. The details of connecting the lever apparatus to the three terminal plug so that the specimen attached to the plug can be screwed into the pressure cylinder as one self-contained piece offer no difficulties of design, and need not be shown.

The apparatus as shown is flexible enough to be adapted to a wide variety of sorts of specimens. Variations in the diameter of the specimen may be allowed for either by making different steel caps, or preferably simply by making suitable steel collars to slip around the specimen by which it is held securely in the pointed end pieces. Variations in the length of the specimen are allowed for by changing the length of the dummy piece of iron at H. Specimens used with the apparatus as shown must be stiff enough to support the compressive stress due to the spring on the lever. But the compressibility of wires may also be measured by a simple change that will readily suggest itself, replacing the specimen S by a slotted frame of iron in which is laid the specimen in the form of wire, attached to the frame by a clamp at the lower end, and at the upper end attached to a clamp, which is in turn attached to the surrounding envelope by a pin. The wire is thus put under tension instead of compression. Measurements may be made on wires of any diameter large enough to stand the necessary tension. One must of course be sure that the elongation of the wire due to the tension of the spring is not large enough compared with the relative deformations produced by pressure to introduce any such complication as might arise from a change in Young's modulus under pressure. A simple calculation will enable one to stay on the safe side of this requirement.

The magnifying power of the lever had to be determined by a special arrangement, it not being possible to measure the dimensions directly accurately enough. An arrangement was made by which a micrometer screw could advance the short arm of the lever by a known small amount, the micrometer screw being provided with a vernier scale permitting readings to 1/20°. The accuracy obtainable with the special arrangement was considerably better than 1/10%.

For specimens whose compressibility was fairly high compared with that of iron the complications of the lever were dispensed with, and the relative change of length was measured directly by a wire attached directly to the end of the specimen. This is shown in Figure 3. The specimen is compressed against the lower end of the iron container by a spring M and also is pressed against the sliding contact D by a spring N.

The final measurements of compressibility were made with one or the other of three different pieces of apparatus; two of these magnified the motion with levers, one having a long envelope for long specimens (maximum capacity 16.5 cm.), and the other a short envelope for pieces of a maximum length of 2.5 cm. The third apparatus was for the direct measurement of the relative change of length, as described in the preceding paragraph.

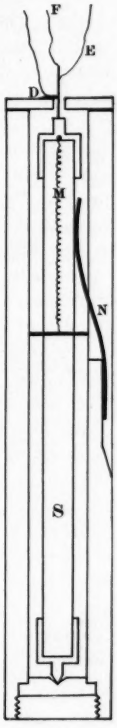

FIG. 3.

Each form of apparatus was checked by making with it blank runs, using as the specimen a piece of the same iron as that whose absolute linear compressibility was measured with the other apparatus. If the compressibility of the envelope (which was made of commercial bessemer steel) was the same as that of pure iron, and if it were perfectly homogeneous, so that it experienced a volume compression without change of figure, then the changes of resistance of the wire under pressure should be such that when the various corrections were applied for the change in specific resistance of the wire under pressure, etc., there should be indicated no outstanding relative motion of specimen and surrounding envelope. Of course for one thing the compressibility of the pure iron and the bessemer steel was probably not exactly the same, so that perfect agreement was not to be expected, but nevertheless the correction so determined due to all these possible sources was very small indeed, and was about that due to the relative compression of the iron and the mica washers (which were 0.012 cm. thick) by which the fixed contact D was insulated. It is to be noticed that after this correction was applied the results gave accurately the difference

FIGURE 3. Device with sliding electrical contact for the direct measurement of the difference of linear compressibility between iron and the specimen S.

of compressibility between the specimen and pure iron, independent of any imperfections in the apparatus, which were thereby eliminated. Except for the convenience of using small corrections, it would have been quite possible to have made the envelope of some other metal, such as brass.

Besides the empirically determined correction just discussed a number of other corrections have to be applied for the change of resistance of the nichrome wire under pressure, for the difference of compressibility between nichrome and iron, and for the temperature effects. These corrections are essentially the same as those needed in getting the absolute linear compressibility of iron, and will not be separately discussed; they are small and involve no difficulty. The data requisite for making these corrections were determined by direct experiment. For those substances whose compressibility is near to that of iron the percentage magnitude of the correction on the difference of compressibility may of course be greater than in the experiment on the absolute linear compressibility of iron. The percentage magnitude of the corrections is approximately inversely proportional to the difference of compressibility.

The total motion of the wire was in all cases small, being seldom more than a small fraction of a millimeter. It will of course be understood that in dealing with such small quantities every feature of the design had to be carefully thought out, and that the apparatus as finally used embodied many details whose best form was found only after several trials, but which it will not be profitable to describe here. Many changes were made in several different pieces of apparatus, and readings were made continuously over a period of four months before the design used for the final measurements here recorded was attained. By far the most trouble was found with the lever apparatus. It is sufficient to mention here that the feature requiring the greatest care is the construction of the bearing points and seats of the lever. These must be of the greatest geometrical perfection, and highly polished, and will repay a considerable amount of labor. The radius of the bearing point must not be too small or the point will break, hence the necessity for a high polish. The result of failure to get proper bearing points is irregularity in the readings; the observations skip erratically about, or often show systematic departures from the correct course for considerable successions of readings.

The pressure was determined, as in all this work, from the changes in the resistance of a coil of manganin wire, and the corrections have been discussed in detail previously.[7] During the course of the work

the coil was calibrated against the freezing point of mercury at 0° at sufficient intervals to insure the accuracy of the pressure measurements.

After the readings had been made of the potentiometer setting as a function of pressure over the entire pressure range, and the various corrections applied to these readings, the points were plotted, potentiometer setting against pressure. This plot is nearly a straight line. A straight line was now passed by computation through the zero point and the point at the highest pressure, and the intermediate points on the line computed corresponding to the intermediate observed pressures. It was necessary to use computation for the intermediate points, as graphical construction would not have been accurate enough. The difference between the linear values and those actually observed was now found by subtraction, and these differences were plotted on an enlarged scale. A smooth curve was now passed through these difference points. This curve could be drawn with sufficient accuracy in most cases free hand. In most cases this curve was symmetrical about the mean pressure (6000 kg.), and could be represented within the limits of error by a parabolic formula. This means that within the limits of error the change of volume is given by a two constant formula of the type used for iron above, namely $\frac{\Delta V}{V_0} = -(a + bp)p$. The change of volume under 12000 kg. was next computed, using as the most probable value of the change of resistance that obtained from the smoothed curve of departures from linearity. In computing this change of volume all the corrections were applied. The initial rate at which the volume changes with pressure was also computed. This initial rate was the average rate to 12000 corrected by a factor obtained from the smoothed difference curve. The correction factor was usually given with sufficient accuracy by doubling the ratio of the deviation at the mean pressure to the mean ordinate, and applying the result as a correction factor to the average rate to 12000. If the deviation from linearity was so great as to make this procedure inaccurate, the change of volume was calculated directly at several intermediate pressures. Having thus obtained the initial rate of change of volume, and the change under 12000, the constants of a formula like that above were at once determined. For several substances, particularly sodium and potassium, the deviation from linearity was so great that it was necessary to calculate from the smoothed curve the changes of volume at even thousand intervals of pressure, and tabulate these, instead of trying to reproduce the results by a single formula.

The procedure in making the calculations outlined in the paragraph above was applied independently at the two temperatures 30° and 75°. Departure from linearity was in most cases so small that it was useless to attempt to try to get the temperature coefficient of the departure. Accordingly in the calculations the mean of the departures found independently at the two temperatures was usually used as that most probably accurate.

The behavior of the metals under pressure gives in many cases a useful check on their probable homogeneity and therefore on the equality of their compressibility in all directions. If the metal is under no internal strains, the relation between deformation and pressure should be single valued, without hysteresis, and there should be no permanent change of dimensions, even after the first application of pressure. The absence of hysteresis could of course be checked by the readings themselves, but the freedom from set on the initial application of pressure was not so easy to determine, because there were sometimes slight initial irregularities in the apparatus itself which were smoothed out by the initial application of pressure. In all cases the metal was subjected to a preliminary application of pressure over the entire range before readings were begun, and the change of zero produced by this preliminary application was also recorded. This should give an upper limit to any actual change of dimensions produced in the specimen by pressure. If the substance is carefully prepared there should be no change, and this was in almost every case the fact. It was possible to make castings of lead, for example, that showed no perceptible permanent change of length after the initial application of 12000 kg. In one or two cases, however, there were comparatively large changes, and these were usually accompanied by hysteresis on subsequent applications of pressure, showing internal strains. These cases will be described in detail later.

There follows now the detailed presentation of data. First are given those metals crystallizing in the cubic system. There are included here a few metals whose structure has not yet been determined, since the chances are that any metal selected at random is cubic. The metals are arranged in order of compressibility, beginning with tungsten, the least compressible. After this are given data for several metals not crystallizing in the cubic system. The work on these latter metals must be extended. The present data are competent to give only an idea of the amount of variation to be expected in the compressibility in different directions.

METALS CRYSTALLIZING IN THE CUBIC SYSTEM.

Tungsten. It is well known that, because of its methods of preparation, this metal may show considerable differences of density, depending on the amount of mechanical working to which it has been subjected, the finer wires having the greater density. It therefore seemed to me desirable to measure the compressibility of two samples differing considerably in the amount of working to which they had been subjected. Through the kindness of the General Electric Company I obtained a number of samples of pure tungsten, and selected two from these best adapted to the measurements. The first was 0.48 cm. in diameter; it had been swaged to these dimensions from the original sintered bar, but had not been drawn through dies. It was mounted as a compression specimen in the lever apparatus, with a length of 8.68 cm. The density at room temperature was found by weighing in air and water to be 19.137. The second specimen was of drawn wire 0.051 cm. in diameter, and was mounted as a tension specimen in the lever apparatus. The length was about 10 cm. The density of this small sample could not be determined with sufficient accuracy by weighing, but tables compiled by the General Electric Company show that the density to be expected on the average for wire of this diameter is 19.48. The difference between the densities of the two samples is thus considerable; it is questionable how much is due to closing of the pores and how much is due to the breaking up of the crystalline structure by working, replacing the crystalline material by amorphous.

Regular readings were made on these two samples at 30° and 75°. The readings were very satisfactory, considering the small compressibility of this metal. Discarding the 8 most irregular points, the average numerical departure from a smooth curve of the remaining 48 points was 0.28% of the effect produced by the maximum pressure. The accuracy of the readings with the two different samples was essentially the same. The departure of the points from linearity, as compared with iron, was well marked, and at the mean pressure was about 2.5 times as great as the average error of a single observation. The deviations from linearity determined for each sample independently from the series of readings at the two temperatures differed by not more than 10% from the mean. The direction of this departure from linearity was such as to make the change of compressibility of tungsten with pressure less than that of iron, as would be expected from its

smaller absolute compressibility. The final results are expressed in the following formulas, p being in kg/cm^2:

$$\text{Swaged rod, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(2.93 - 1.5 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(2.95 - 1.5 \times 10^{-5}p)\,p$$

$$\text{Drawn wire, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(3.15 - 1.6 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(3.16 - 1.5 \times 10^{-5}p)\,p.$$

It is perhaps not to be expected that the drawn wire with the greater density should also have the greater compressibility. This is possibly due in part to the greater amount of the amorphous metal that the drawn wire doubtless contains, since it is usually true that an amorphous phase is more compressible than the corresponding crystalline one.

The only previous determination of the compressibility of tungsten seems to be by Richards.[1] His material was in the form of fused buttons, also obtained from the General Electric Company, and had a density at room temperature of 19.231. He finds for the initial compressibility 2.7×10^{-7}. The value is given to only two significant figures, and I gather from personal conversation with Professor Richards that he regards as possible an error of several units in the last place.

Platinum. Runs were made on two specimens, of quite different dimensions, in two different pieces of apparatus. I am indebted to the kindness of Baker and Company for the loan of the two specimens. The material was stated by them to be chemically pure platinum. The first specimen was 2.5 cm. long and 0.8 cm. in diameter. It was used as a compression specimen in the lever apparatus for short specimens. It was cut from a drawn rod of platinum, and before the measurements was annealed for several hours in an electric furnace at a temperature of 800°. The second specimen was of drawn wire, annealed, 0.065 cm. in diameter and about 10 cm. long, and was mounted as a tension specimen in the lever apparatus for long specimens.

The regular set of readings at two temperatures was made on each specimen. The readings with the shorter specimen were not

nearly as regular as those with the longer wire, which indeed is not surprising in view of the smallness of the effect. The average arithmetical departure from a smooth curve of the 28 observed points with the short specimen (no discards) was 2% of the maximum pressure effect, and the departure from linearity, which was perfectly well marked, was 3% at the maximum. The series of readings at the two temperatures gave the same departure from linearity to one significant figure. It is obvious that a high degree of precision cannot be expected for the pressure coefficient of compressibility of this specimen. The average arithmetical departure from the smooth curve of all the readings on the wire (no discards) was 0.7% of the maximum pressure effect, but here the deviation from linearity, although perfectly evident, was only two thirds as great as the error of a single reading. The deviation from linearity at the higher temperature was about 50% greater than at the lower. The average value of the compressibility obtained from the wire sample may be expected to be relatively more accurate than that obtained from the massive specimen, but the differences are beyond the errors of the measurements, and point to a real difference between the two specimens. The pressure coefficient of the difference of compressibility between iron and platinum cannot obviously claim any great accuracy, but the actual pressure coefficient, obtained by combining these readings with the absolute values for iron, may be expected to be somewhat more accurate.

The results found are reproduced by the following formulas:

$$\text{Wire, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(3.60 - 1.8 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(3.64 - 1.8 \times 10^{-5}p)\,p$$

$$\text{Rod, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(3.05 - 0.0 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(3.09 - 0.0 \times 10^{-5}p)\,p.$$

It is of course not likely that the compressibility of the rod actually does not change with the pressure, but at any rate the change is small.

The initial compressibility of platinum has been found by Richards to be 3.7×10^{-7}. The agreement with the value found above for the wire is well within the limits of error. Richards also obtained his material from Baker and Company. He found for the density at 20°

21.31. The density of the larger of the two pieces measured above was 21.34 at 20°. Evidently the mechanical condition of these two specimens must have been nearly the same.

Molybdenum. The treatment of molybdenum was like that of tungsten. Through the kindness of the General Electric Company I obtained a number of pieces in different stages of mechanical working; the compressibility of two of these was measured. One specimen, which had been swaged only but not drawn, was used as a compression specimen in the lever apparatus; its diameter was 0.48 cm. and length about 10 cm. This specimen was in two pieces, held butting end to end in a steel sleeve. It is often possible in this way to fit together several shorter pieces and obtain effectively a longer piece, thus increasing the accuracy of the measurements. The density of this specimen at 20° was found by weighing to be 10.185. The second specimen was in the form of drawn wire 0.051 cm. in diameter and 10 cm. long, mounted as a tension specimen in the lever apparatus. Its density could not be obtained with sufficient accuracy by weighing, but the average density found by the General Electric Company for wire of this diameter is 10.20.

The regular series of runs, at 30° and 75°, were made for each specimen. The accuracy of the measurements was about the same for the two specimens. Discarding 5 points, the average arithmetical departure from a smooth curve of the remaining 50 points was 0.36% of the maximum pressure effect, and the departure from linearity (that is, the departure from linearity of the difference of compressibility of iron and molybdenum) was 1.40% of the maximum pressure effect. The departure from linearity of each specimen was sensibly the same at the two temperatures. The final results are:

$$\text{Swaged rod,} \quad \text{At } 30° \; \frac{\Delta V}{V_0} = -10^{-7}(3.47 - 1.2\,p)\,p$$

$$\text{At } 75° \; \frac{\Delta V}{V_0} = -10^{-7}(3.48 - 1.2\,p)\,p$$

$$\text{Drawn wire,} \quad \text{At } 30° \; \frac{\Delta V}{V_0} = -10^{-7}(3.61 - 1.0\,p)\,p$$

$$\text{At } 75° \; \frac{\Delta V}{V_0} = -10^{-7}(3.62 - 1.0\,p)\,p\,.$$

The compressibility of the drawn wire is seen to be higher than that of the swaged rod in spite of its higher density, as was also the case for tungsten, and probably for the same reason.

Richards has found for the initial compressibility of molybdenum in the form of fused buttons of density 10.21 the value 4.5×10^{-7}. This again is considerably higher than the value found above, but the discrepancy is not more than is to be expected when the small size of Richards' sample is considered, and the fact that one of his two results was 40% higher than the other. Richards' object in his measurement was only to obtain the order of magnitude.

Tantalum. This was in the form of a drawn wire 0.062 cm. in diameter and 10 cm. long, mounted as a tension specimen in the lever apparatus. I am indebted for this material to the kindness of the Fansteel Co., of North Chicago. It was stated by them to be of unusually high purity, but I have no analysis. As a partial means of estimating its purity I determined its temperature coefficient of resistance between 0° and 100°. The relation between temperature and resistance is sensibly linear over this range, and the average coefficient is 0.00335. This is materially higher than the coefficient of a piece which I had formerly obtained from the General Electric Company, namely 0.00293, and for which I have determined the effect of pressure on electrical resistance. The coefficient is less than that of a sample of Holborn,[8] 0.00347.

Two runs were made on this specimen, as usual, at 30° and 75°. The results at 30° were appreciably more regular than at 75°. At 30° the average arithmetical departure of the observed points from a smooth curve (no discards) was 1.4% of the maximum pressure effect, and at 75° it was 3.2%. The departure from linearity was sensibly the same at the two temperatures, and at its maximum was 6.8% of the pressure effect. It must be remembered that because of the small difference of compressibility between tantalum and iron a large percentage error in the difference of the two compressibilities need not mean a large error on the absolute compressibility.

The final results are given by the formulas:

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(4.79 - 0.25 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(4.92 - 0.25 \times 10^{-5} p)\, p.$$

The close approach of the compressibility to constancy with pressure is to be noted.

The compressibility of tantalum at 20° over a small pressure range

has been found by Richards to be 5.2×10^{-7}. His material was from the General Electric Company, and was in the form of fused buttons.

Palladium. Runs were made on two different samples, both of which I owe to the kindness of Baker and Company. They were said to be of the highest attainable purity, but I have no analysis. One of these was a massive specimen, 0.75 cm. in diameter and 2.5 cm. long. It was used as a compression specimen in the lever apparatus for short specimens. The second was in the form of wire, 0.062 cm. in diameter, 10 cm. long, and was mounted as a tension specimen in the lever apparatus for long specimens. Each sample was annealed after receiving from Baker, the massive specimen by heating to 800° for two hours in an electric furnace and slowly cooling, and the wire by heating in a Bunsen burner to a bright red. Two regular runs, at 30° and 75°, were made on each specimen.

The average arithmetical departure of the readings of the massive specimen from a smooth curve (no discards) was 2.2% of the maximum pressure effect. It was not possible to detect any departure from linearity. For the wire the average arithmetical departure was 3.0% of the maximum pressure effect, and again there was no detectible departure from linearity. The final results found for these two specimens are:

$$\text{Massive specimen, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.19 - 2.1 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.11 - 2.0 \times 10^{-5} p)\, p$$

$$\text{Drawn wire, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.28 - 2.1 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.31 - 2.1 \times 10^{-5} p)\, p.$$

It is to be noticed that the temperature coefficient of the massive palladium appears to be negative. This is a very unusual occurrence, and it is to be doubted whether the accuracy of the measurements is so high as to compel the conclusion that this is actually the case.

The initial compressibility of palladium at 20° has been found by Richards to be 5.3×10^{-7}, agreeing perfectly with the value found above for the wire. Richards' material was also obtained from Baker, and was a massive specimen weighing 94 gm. Its density was 12.14, against 11.97 for the massive specimen above.

Nickel. Measurements were made on samples from two sources.

One was a piece of commercial nickel obtained from the International Nickel Company in the form of a drawn bar 0.75 cm. in diameter and 16 cm. long. The purity was high commercial purity, a little better than 99%. It was annealed by heating for several hours to a bright red after its final machining, and was used as a compression specimen in the lever apparatus for long specimens. The second sample piece of nickel was obtained from the research laboratories of the Leeds and Northrup Company, and was of very unusually high purity. It is the same material as that for which I have already published data for the effect of tension on resistance [9] and pressure on thermal conductivity.[10] I have no chemical analysis, but have determined the temperature coefficient of resistance between 0° and 100° to have the mean value 0.00634, which is very high. This material was provided in the form of small cast ingots a couple of mm. thick and 5 or 6 cm. long. There were flaws in these castings large enough to be visible to the eye. I tried to get rid of these flaws by forging the castings to considerably smaller dimensions. The forged castings were mounted as compression specimens in the lever apparatus for long specimens, and their compressibility measured, but there was a rather large permanent set on the first application of pressure, and the relation between pressure and deformation showed a rather large amount of hysteresis. In order to get rid of the effect of the flaws, therefore, this forged piece was drawn down to wire of 0.079 cm. diameter, annealed at a bright red after the last drawing, and used as a tension specimen in the lever apparatus for long specimens.

The regular series of readings were made on each specimen, at 30° and 75°. The average arithmetical deviation from a smooth curve of the readings on the commercial rod (no discards) was 0.8% of the maximum pressure effect. The corresponding average deviation from a smooth curve of the readings on the wire, making three discards (it is usually true that the tension specimens do not give such regular results as the compression specimens) was 1.1% of the maximum effect. Neither specimen showed any perceptible deviation from linearity, which means of course that the variation of compressibility with pressure is the same for nickel as for iron.

The final results are as follows:

Commercial rod, At 30° $\frac{\Delta V}{V_0} = -10^{-7}(5.25 - 2.1 \times 10^{-5}p)\,p$

At 75° $\frac{\Delta V}{V_0} = -10^{-7}(5.28 - 2.1 \times 10^{-5}p)\,p$

$$\text{Pure drawn wire, At } 30^\circ \quad \frac{\Delta V}{V_0} = -10^{-7}(5.29 - 2.1 \times 10^{-5}p)\,p$$

$$\text{At } 75^\circ \quad \frac{\Delta V}{V_0} = -10^{-7}(5.35 - 2.1 \times 10^{-5}p)\,p.$$

A rough value for the average compressibility to 12000 kg. of the forging of pure nickel was 5.16×10^{-7}.

The values above for the two samples are seen to be nearly the same, and it is therefore probable that the usual impurities, such as cobalt and iron, have little effect on the compressibility.

The initial compressibility has been found by Richards to be 4.3×10^{-7}. His material was in the form of cubes, in which the pure metal is often supplied by chemical houses. Richards states that the nickel as originally provided was full of flaws into which the mercury was forced by pressure, and that the effect of these flaws was got rid of by heavy forging. My experience with the cast specimen above would strongly indicate (because of the hysteresis shown by this sample) that the forging must have introduced considerable internal strain, which is doubtless responsible for Richards' low value. The effects of hysteresis would be especially pronounced over a small pressure range, and would be in the direction to account for Richards' low value.

Cobalt. This I owe to the kindness of Professor C. C. Bidwell of Cornell University, by whom it was in turn obtained from Dr. Herbert T. Kalmus, who had prepared it for the Canadian Government. It was of high purity, and had the following analysis: Fe 0.14, Ni 0.00, S 0.019, Si 0.02, C 0.09, Co 99.73. It was in the form of wire about 0.075 cm. in diameter and 6 cm. long, and was mounted as a tension specimen in the lever apparatus for long specimens. The material had been formed into wire by swaging followed by drawing at a red heat. It was not perfectly straight as supplied. It is rather brittle to bending, but I was able to make it perfectly straight by rolling it between red hot iron plates, thus at the same time annealing it.

The two usual runs at 30° and 75° were made. The results were gratifyingly regular, considering the smallness of the effect. The average arithmetical departure from a straight line of the 28 readings (no discards) was 1.3% of the maximum pressure effect; 1.3% on the difference of compressibility means 0.1% on the actual compressibility. It was not possible to detect any departure from linearity.

The final results are expressed by the formulas:

$$\text{At } 30^\circ \quad \frac{\Delta V}{V_0} = -10^{-7}(5.39 - 2.1 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.47 - 2.1 \times 10^{-5}p)\, p.$$

As far as I can find, the compressibility of cobalt has not been previously measured. The value found above, close to that for nickel and iron, is of the order of magnitude that one would expect.

Nichrome. The reason for determining the compressibility of this alloy is that the difference of compressibility between it and iron enters as a correction on the observed readings. The correction is very small, and at the maximum amounts to only 0.3 mm. on the slide wire of the potentiometer. The material was obtained from Driver Harris Company, and is of the grade known as Nichrome II. Its composition is Ni 80% and Cr 20%. The sample measured was from the same length as the wires attached to the lever or the specimen, by which the relative changes of length were measured. Its diameter was 0.030 cm. and length about 10 cm. It was mounted as a tension specimen in the lever apparatus for long specimens.

Because of the smallness of the correction it was necessary to measure the compressibility only at 30°. Here the mean departure from a smooth curve (no discards) was 1.5% of the maximum pressure effect, which corresponds to 0.09% on the actual compressibility. The deviation from linearity was sensibly not the same as for iron, and at the maximum was 5.5% of the maximum pressure effect. The results are contained in the formulas:

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.50 - 1.5 \times 10^{-5}p)\, p.$$

Gold. Measurements were made on two samples, both of which I owe to the kindness of Baker and Company. The specimens were stated to be of the highest purity, but I have no analysis. The density was found to be 19.272 at room temperature. Both specimens were in the form of drawn rod 0.75 cm. in diameter, and were annealed at a bright red before the measurements. The first was 2.5 cm. long, and was mounted as a compression specimen in the lever apparatus for short specimens; the second was 12 cm. long, and was mounted as a compression specimen in the lever apparatus for long specimens.

The compressibility of gold is exceedingly close to that of iron, and hence accurate results are not to be expected for the difference of compressibility. Apart, however, from the smallness of the effect, the apparatus did not function as well as usual during these measurements, there being minor electrical troubles, probably due to short circuits,

so that it was necessary to repeat some of the readings. Four sets of readings were made on the shorter sample, two at 30° and two at 75°, and three sets on the longer sample, one at 30° and two at 75°. The readings on the short sample at 75° were never satisfactory, and those on the long sample at 75° left much to be desired. The readings at 30° were fairly satisfactory.

At 30° the average arithmetical deviation from a smooth line of the readings on the short sample was 5% of the maximum pressure effect. For the long sample the deviation at 30° averaged 5.9% and at 75° 4.2%. The results are given by the formulas:

$$\text{Short sample,} \quad \text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.84 - 2.1 \times 10^{-5}p)\,p$$

$$\text{Long sample,} \quad \text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.77 - 3.1 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(5.70 - 2.1 \times 10^{-5}p)\,p.$$

The details of the variation of the coefficients in these formulas probably are not accurate. Because of its greater length the results for the long sample are doubtless to be preferred. Probably the safest conclusion to draw from these measurements on gold is merely that at 30° the average compressibility to 12000 is approximately 5.40×10^{-7}, and at 75° it is 5.45×10^{-7}.

The compressibility of gold has been measured both by Richards and A. W. J. Richards finds the initial compressibility at 20° of gold of density 19.24 to be 6.3×10^{-7}, and A. W. J. find the compressibility to be constant with pressure, and its value over the range of 12000 kg. to be 5.6×10^{-7}. It is to be noticed that Richards makes gold more compressible than iron, and A. W. J. less. The measurements of this paper would seem to leave no room for doubt that it is actually less than iron. It is to be noticed that A. W. J. used a constant value for the compressibility of iron, namely 5.9×10^{-7}. If for this is substituted the new value found above for the average compressibility over the range of 12000, namely 5.62×10^{-7}, A. W. J.'s value becomes 5.3×10^{-7}, agreeing within one unit in their last significant figure with the value found above. It is possible that the high value of Richards is due to the fact that his gold was not annealed after the final drawing; the difference is in the same direction as produced by a similar effect in tungsten and molybdenum.

The low value of the compressibility of gold is somewhat surprising

both when one considers the mechanical softness of the metal, and also that its position in the periodic table below copper and silver suggests a compressibility following the succession of values of these two other metals, which would lead to a figure more than twice as high as the actual one.

Copper. Copper from two sources was used. One was commercial drawn rod 0.6 cm. in diameter. Two sets of runs were made with this, the first with the rod in the commercial drawn condition, and the second after annealing. The second grade of material was pure copper from the Bureau of Standards, cut from one of their melting point samples, and had the following analysis: Sb 0.004, As 0.0026, S 0.0026, Cu 99.987. This second sample was measured only in the annealed condition. Both samples were mounted as compression specimens in the lever apparatus for long specimens; it was necessary to dowel together two pieces of the pure copper in order to get the requisite length, which was 12 cm. In addition to the runs on these long samples, at least four runs were made with preliminary forms of apparatus on shorter samples of the pure copper. The accuracy was not as high as in the final runs, and it is not necessary to describe the details, but within the somewhat wider limits of error, the results of these preliminary measurements agreed with the final results. It was during the preliminary measurements that an attempt was made to find a difference of compressibility of copper in different directions, with negative results.

The commercial copper was quite unusual in that it showed evidence of internal strains. The readings both before and after the annealing were affected by considerable hysteresis, and after the annealing the first application of pressure produced a rather large permanent distortion. The average arithmetical deviation from a smooth curve of the results for the unannealed copper (two discards) was 2.6 % of the maximum pressure effect. Almost the entire amount of this deviation is due, not to irregularity of the individual points, but to hysteresis, which at the maximum was 5.5% of the maximum pressure effect. For the commercial annealed copper the average arithmetical deviation from smoothness was 1.6% of the maximum effect, and the greatest width of the hysteresis loop was 5.5%. The loop was of a different shape from that of the unannealed copper. The pure copper from the Bureau of Standards showed no hysteresis; the average arithmetical departure (no discards) from a smooth curve was 0.47%, and the maximum departure from linearity was 1.44%. The results are contained in the following formulas:

Commercial drawn rod, unannealed,

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(7.32 - 2.7 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(7.39 - 2.7 \times 10^{-5}p)\,p\,.$$

Same commercial rod, annealed,

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(7.29 - 2.7 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(7.37 - 2.7 \times 10^{-5}p)\,p\,.$$

Pure copper,

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(7.19 - 2.6 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(7.34 - 2.7 \times 10^{-5}p)\,p.$$

Richards has found the initial compressibility at 20° to be 7.4×10^{-7}. A. W. J. could find no departure from linearity. Correcting their results for the new value for iron, their average compressibility to 10000 was 7.1×10^{-7}, against 6.84×10^{-7} given by the formula above for pure copper.

Uranium. I am indebted for this to the kindness of Dr. A. W. Hull of the General Electric Company. It was furnished in the form of rolled strip 0.05 cm. thick, 0.6 cm. wide, and 5 cm. long. I have no chemical analysis. The temperature coefficient of the electrical resistance between 0° and 100° was 0.0022. Because there are no other measurements at present on the electrical properties of uranium, this does not mean much as to the purity, except that probably the purity was not high, but if in the future the properties of pure uranium are measured, this coefficient should give more definite information. This sample was mounted as a tension specimen in the lever apparatus for long specimens.

The usual two runs were made, at 30° and 75°. The average arithmetical departure from a smooth curve of all 28 points (no discards) was 1.0% of the maximum pressure effect. The average deviation at 75° was two or three times as great as at 30°. The maximum departure from linearity was 0.59% of the maximum pressure effect. It is therefore evident that the accuracy of the departure

of the difference of compressibility between uranium and iron is not high. The results are embodied in the formulas:

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(9.66 - 2.5 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(9.55 - 2.2 \times 10^{-5} p)\, p.$$

It is to be noticed that the temperature coefficient of compressibility seems to be negative. This is unusual, and perhaps is not genuine, but I give the results as they were found because the magnitude of this temperature effect is greater than the probable error.

The compressibility of uranium seems not to have been previously measured. The value found is not inconsistent with that which might be expected from its position in the periodic table, but this is always a rather inaccurate way of getting compressibility, and in the case of uranium, because of its position at the end of the list of the elements, it is a particularly poor way of guessing the compressibility.

Silver. This I owe to the courtesy of Baker and Co. I have no analysis, but it was said to be of the highest possible purity. It was provided in the form of drawn rod 0.6 cm. in diameter and 12 cm. long. It was annealed at a red heat before the measurements, and mounted as a compression specimen in the lever apparatus for long specimens. The density at 20° was 10.486. I also made measurements on another similar piece of material in the lever apparatus for short specimens. This was done before the final improvements had been made in the apparatus, and the results were rather irregular, but agree with those found for the other specimen within the limits of error.

The regular two runs at 30° and 75° were made. The average arithmetical departure from a smooth curve of the 28 readings (no discards) was 0.48% of the maximum pressure effect. The maximum departure from linearity, which was sensibly the same at the two temperatures, was 2.05%. The final results are given by the formulas;

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(9.87 - 4.4 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(10.04 - 4.5 \times 10^{-5} p)\, p.$$

The initial compressibility found by Richards for silver of density 10.5 was 9.9×10^{-7}. A. W. J. found no departure from linearity with

pressure; their mean value, corrected for the new value for iron, was 9.4×10^{-7}, both results agree very closely with the value above.

Aluminum. For these measurements I was fortunate to obtain two samples of exceptionally high purity. One was in the shape of a hard drawn rod and the other a casting, both 1.3 cm. in diameter. The density of both specimens at atmospheric temperature was the same, 2.700. The analysis of both specimens was also the same: Si 0.008, Fe, 0.013, Cu 0.014, Mn Nil, Al (by diff.) 99.965. For measurements these pieces were turned to a diameter of 0.6 cm., and were mounted as compression specimens in the lever apparatus for long specimens. The length of the casting was 7 cm. and that of the drawn piece 12 cm.

By way of curiosity I made measurements on the hard drawn piece first before annealing. I expected hysteresis and other evidence of internal stress, but to my surprise the results were perfectly smooth and gave evidence of nothing of the sort. These measurements were made only at one temperature and to a maximum pressure of 10000 instead of 12000, there being some temporary trouble with the pressure apparatus. This hard drawn piece was then annealed at 300° for several hours, and then the regular series of runs at 30° and 75° was made. The average arithmetical departure from a smooth curve of the 28 observed points (one discard) was 0.3% of the maximum pressure effect, and the maximum departure from linearity was 0.75%. The departure from linearity seemed to be somewhat greater at 30° than at 75°, but on the other hand the accuracy of the readings at 30° was materially greater than at 75°. The mean of the departures found at the two temperatures was used in the final computations.

The cast specimen was used without annealing; it showed no hysteresis or other evidence of internal strain. The average arithmetical departure from a smooth curve of the 28 observed points (one discard) was 0.3%, and the maximum departure from linearity 1.43%. The deviation from linearity was exactly the same at both temperatures, and this quantity seemed to be given much more satisfactorily by the measurements on the casting than by those on the drawn rod.

Besides the runs just described, at least six other complete sets of runs were made on aluminum, mostly with shorter specimens. A number of the preliminary forms of apparatus were tested by measuring with them the compressibility of aluminum. These early results were of course less accurate than the final ones, but agreed with them within the wider limits of error.

The final results are given by the formulas:

Drawn rod, Hard, At 30° $\frac{\Delta V}{V_0} = -10^{-7}(13.40 - 3.5 \times 10^{-5} p)\, p$

Drawn rod, annealed, At 30° $\frac{\Delta V}{V_0} = -10^{-7}(13.34 - 3.5 \times 10^{-5} p)\, p$

At 75° $\frac{\Delta V}{V_0} = -10^{-7}(13.91 - 3.5 \times 10^{-5} p)\, p$

Casting At 30° $\frac{\Delta V}{V_0} = -10^{-7}(13.43 - 5.0 \times 10^{-5} p)\, p$

At 75° $\frac{\Delta V}{V_0} = -10^{-7}(13.76 - 5.1 \times 10^{-5} p)\, p.$

Some time ago I found the average compressibility to 6000 kg. of a piece of commercial aluminum rod to be 11.7×10^{-7}, distinctly lower than the values found above. These early readings were not accurate enough to show a departure from linearity. The specimen showed set on the initial application of pressure, but otherwise there was no evidence, such as hysteresis, of internal strain. Richards has found the compressibility of aluminum of unstated analysis of density 2.60 to be 14.1×10^{-7}, somewhat higher than the above. A. W. J. for aluminum containing 0.235% Si and 0.016% Fe were not able to detect any departure from linearity over the range of 12000 kg., and give for the average compressibility (corrected by my new value for iron) 12.7×10^{-7}, which agrees to the third figure with the value given by the above formula for cast aluminum.

Germanium. The crystal structure of this substance has not yet been published; I owe to the kindness of Dr. A. W. Hull of the General Electric Company the information given in personal correspondence that X-ray analysis shows it to be cubic, of the same type of lattice as diamond and silicon.

For the sample of germanium I am indebted to the kindness of Professor C. C. Bidwell of Cornell University, who in turn obtained it from Professor L. M. Dennis of the Cornell Chemistry Department. It is the same specimen as that whose electrical properties he has reported in the Physical Review.[11] The material is evidently abnormal in some way, because the electrical resistance behaves normally below 100°, but above 100° decreases instead of increasing with rising temperature. The specimen was in the form of a casting about 2.5

cm. long and of square section, 0.5 cm. on the diagonal. Its density at 20° was 5.302. It was mounted as a compression specimen in the lever apparatus for short specimens. The compressibility measurements, as well as those on electrical resistance, showed that their is something abnormal about this substance. At 30° the points with increasing pressure lay regularly on a smooth curve, but at the maximum pressure there was an abrupt displacement corresponding to a shortening by an amount 7% of the maximum pressure shortening, and the subsequent points lay on another smooth curve displaced by this amount. The points at 75° showed no irregularity. On taking the apparatus apart, I found that one of the corners of the specimen was broken off. The abrupt displacement was ascribed to the breaking off of this chip, and no more was thought of it. The fractured material is more like a glass in appearance than a metal. Several days later, the specimen meanwhile having rested quietly wrapped in tissue paper, I found that one end of the specimen had spontaneously fractured into a great many small pieces, as badly annealed glass does sometimes under internal strain. It suggests itself that there may be another polymorphic modification at high pressures, the transition not being sharp, but viscous, and that it may have been the internal strains produced by the gradual transformation of this new modification that caused the fracture.

Making correction for the displacement from one smooth curve to another, the average arithmetical departure from a smooth curve of the 28 readings at both temperatures (no discards) was 0.33%, and the maximum deviation from linearity was 2.1% of the maximum pressure effect. There was no difference detectible between the deviations from linearity at the two temperatures.

The final results are given by the formulas:

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(13.78 - 6.8 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(13.64 - 6.8 \times 10^{-5}p)\,p.$$

Again we find a compressibility less at the higher temperature. The variation with temperature seems to be well beyond the experimental error, and perhaps is not surprising in view of the abnormal behavior of the electrical resistance of this substance at higher temperatures.

There seem to be no previous measurements of compressibility.

Lead. This material was a melting point sample from the Bureau of Standards. The analysis of this specimen had not been completed. A presumably similar piece of purity 99.9948 is reported in detail in a previous paper.[12] Two samples were prepared in two different ways. The first was cast in a graphite mold, and chilled by lowering the mold slowly into water while the upper part of the casting was kept hot, in this way ensuring solidification from the bottom up without the formation of flaws. This was seasoned by heating in oil to 200° after casting. Its density at 20° was 11.347. It was machined to 0.75 cm. diameter and 16 cm. long, and was mounted in the apparatus for direct measurement without multiplication. The second piece was cast like the first, then extruded cold from a diameter of 1.5 to 0.75 cm., annealed at 230°, and measured in the same apparatus as the first piece. Its density at 20° was 11.337. Neither specimen showed any perceptible permanent set even after the first application of pressure.

Regular runs were made on each sample at 30° and 75°. The cast sample gave points whose arithmetical departure from a smooth curve (no discards) was 0.14%, and the maximum departure from linearity averaged 3.1%. The average arithmetical departure from a smooth curve of the points for the extruded sample (no discards) was 0.22%, and the maximum deviation from linearity was 2.2%. It is remarkable that both samples agreed in showing a departure from linearity nearly 50% greater at the lower temperature, but this seemed to me so unlikely, that I have preferred to regard it as due to a chance accumulation of error, and have used the mean of the deviations at the two temperatures in computing the final formulas, which are:

Casting,

$$\text{At } 30^\circ \quad \frac{\Delta V}{V_0} = -10^{-7}(23.73 - 17.25 \times 10^{-5}p)\,p$$

$$\text{At } 75^\circ \quad \frac{\Delta V}{V_0} = -10^{-7}(24.33 - 17.7 \times 10^{-5}p)\,p$$

Extruded casting

$$\text{At } 30^\circ \quad \frac{\Delta V}{V_0} = -10^{-7}(23.05 - 12.3 \times 10^{-5}p)\,p$$

$$\text{At } 75^\circ \quad \frac{\Delta V}{V_0} = -10^{-7}(23.63 - 12.3 \times 10^{-5}p)\,p.$$

It is to be noticed that these two samples differ chiefly in their pressure coefficient of compressibility; the average compressibility to 12000 kg. of the two samples is practically the same.

The initial compressibility of lead at 20° has been found by Richards to be 22.8×10^{-7}, appreciably smaller than the above. A. W. J. gives for the initial compressibility 21.7×10^{-7}. They also give a value for the decrease of compressibility with pressure, but they find a much smaller decrease than I do. Their decrease of instantaneous compressibility over a range of 10000 kg. (using my new values for the change of compressibility of iron with pressure) would be 1.2×10^{-7}, against a minimum value twice as great from the formulas above. A. W. J.'s average compressibility to 10000 kg. is 21.2×10^{-7} against 21.8 above for either sample.

Thallium. This material was prepared electrolytically by me several years ago, and I have already published data for some of its electrical properties. Judging by the temperature coefficient of resistance, its purity is high. Since the previous work the metal has been kept in a sealed glass tube. The metal was now fused under KCN, the fused button was hammered to fit the extrusion block, and it was extruded from a diameter of 1.2 to 0.6 cm. The final length was 13 cm. This was mounted in the apparatus for direct measurement without magnification. There was no perceptible set on the first application of pressure.

Discarding the three worst points, the average arithmetical deviation from a smooth curve of the remaining 27 points was 0.34%, and the maximum deviation from linearity was 4.0% of the maximum pressure effect. The deviation from linearity is unusually large for thallium, and furthermore it is not symmetrical about the mean pressure, so that the results cannot be represented by a too constant formula. I have therefore computed the change of volume at intervals of 3000 kg. (in terms of the volume at 30° and atmospheric pressure as unity) and give them in the following table.

TABLE I.

CHANGE OF VOLUME OF THALLIUM UNDER PRESSURE.

Pressure kg/cm²	$\Delta V/V_0$ 30°	75°
3000	−.00978	−.01011
6000	.01872	.01908
9000	.02700	.02724
12000	.03505	.03554

Richards gives the initial compressibility of thallium which contained a slight amount of lead as 23×10^{-7}. The initial compressibility may be found graphically from the data of the table just given, or it may be computed. I have passed a three constant power series curve through the points at 3000, 6000, and 9000 kg., and from this find the initial compressibility at 30° to be 34.8, and at 75°, 36.7×10^{-7}. This is so much higher than the value of Richards that it seems difficult to ascribe to experimental error or slight impurity. The crystal structure of thallium does not seem to have been determined as yet; the difference in these values of compressibility strongly suggests that the crystal system cannot be cubic.

Cerium. This material I owe to the kindness of Dr. A. W. Hull of the General Electric Company. It was provided in the form of a square bar. I extruded it at about 400° to a round section 0.3 cm. in diameter, thereby reducing its section about four fold, and obtaining a piece 4.5 cm. long. This was mounted as a compression specimen in the lever apparatus for long specimens. The purity of this specimen was presumably not high, as its mean temperature coefficient of resistance between 0° and 100° was only 0.001, but since the compressibility seems never to have been measured, and impurity usually has only an additive effect on compressibility, I thought it of sufficient interest to run through the measurements.

The two regular runs were made, at 30° and 75°. Because of trouble with the pressure apparatus the maximum pressure of these runs was only 10000 instead of the usual 12000 kg., but it did not seem worth while to go to the labor of repeating the measurements over the greater range. The average departure from a smooth curve of the 23 observed points (no discards) was 0.47%, and the maximum departure from linearity was 2.2% of the maximum pressure effect. The final results are given by the formulas:

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(35.74 - 19.0 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(35.80 - 19.7 \times 10^{-5} p)\, p.$$

This compressibility is not inconsistent with that to be expected for cerium from its position in the periodic table.

Calcium. Material from two sources was used. The first was obtained from the General Electric Company and was cut from the same block 1 inch in diameter as I used for previous determinations

of the density and thermal expansion.[13] This block was perfectly free from any flaws on the exterior, but in cutting it in two preparatory to getting out a smaller specimen, an inclusion of slag was found in the very center. The previous measurement of density must therefore have a small error, and the value for the expansion also an error, but presumably not so large. On making a second cut no new inclusion was found. A clean piece was got from the original cylinder approximately 1.3 cm. in diameter, and this was extruded at a temperature of 450° to 0.6 cm. in diameter. A piece 10.5 cm. long was finally obtained and mounted in the apparatus for direct measurement. Its density at 20° was 1.555 against the previous value 1.556.

The second piece I owe to the kindness of Professor C. C. Bidwell. I do not know the origin, but it was stated to be of unusually high purity. This was originally of roughly square section 1.6 cm. in diameter. It was extruded in two steps at 450°, first to a round section 1.3 cm. in diameter, and then to 0.6 cm. diameter. The final length was the same as that of the other piece, and it was measured in the same apparatus. Its density at 20° was 1.532.

Professor F. A. Saunders was kind enough to make a spectroscopic analysis of these two samples for me, with the following results:

Calcium from General Electric Co.: Sr, considerable, perhaps 1 to 5% (2% would account for the difference of density), Cu trace, Mg trace, Al trace, Si trace.

Calcium from Professor Bidwell; remarkably pure, Mg trace, Cu trace, nothing else.

The regular runs at 30° and 75° were made on each specimen. The average arithmetical departure from a smooth curve of the points from the sample from the General Electric Co. (no discards) was 0.14%, and the maximum departure from linearity was 3.55% of the maximum pressure effect. The corresponding values for the sample of Professor Bidwell were (one discard) 0.11% and 3.7%. In spite of the high compressibility of calcium, the departure from linearity was symmetrical about the mean, so that it is possible to represent the results by a two constant formula. The results follow:

Calcium from General Electric Co.,

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(59.46 - 48.8 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(59.67 - 48.8 \times 10^{-5} p)\, p.$$

Calcium from Professor Bidwell,

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(56.97 - 47.2 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(58.50 - 52.7 \times 10^{-5} p)\, p.$$

The higher temperature coefficient of the second and purer sample is to be noticed; the pressure coefficient of the two samples is about the same.

The initial compressibility of calcium of density 1.54 has been found by Richards to be 56×10^{-7}. This agrees with the value above within the limits of error indicated by Richards' two significant figures.

Strontium. This material was from the same lot most kindly supplied me by Dr. B. L. Glascock as that for which I have previously determined the changes of resistance under pressure.[14] The purity is unusually high. The most homogeneous lump of this lot was chosen, and it was extruded in two stages to a final diameter of 0.3 cm. and machined to a length of 1.1 cm. The extrusion was performed at a temperature of 270° and under oil to avoid chemical action. The sample was mounted as a compression specimen in the lever apparatus for long specimens.

One preliminary run was made, in which it was not possible to reach more than 10,000 kg. because of trouble with the pressure apparatus, and then two regular runs to 12,000 at 30° and 75°. Within the limits of error the results of the first incomplete run agreed with the final results. The average departure of the 28 observed points of the regular runs from a smooth curve (no discards) was 0.35% and the maximum deviation from linearity was 3.9% of the maximum pressure effect. The deviation was the same at the two temperatures. In spite of the high compressibility of strontium the deviation from linearity was symmetrical about the mean pressure, so that it is possible to represent the changes of volume by a two constant formula, which follows:

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(81.87 - 72.5 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(82.68 - 71.7 \times 10^{-5} p)\, p.$$

There seem to be no previous determinations of the compressibility of strontium.

Lithium. This was from Merck, obtained before the war, sealed in glass under oil, and was from the same lot as that used in determining the effect of pressure on resistance. A chemical analysis showed 0.7% Al and a trace of Fe. This was extruded cold to a diameter of 0.6 cm. The original piece was of square section; the extrusion produced little change of section or of length, but only a change in the shape of the section from square to round. The density at 20° was 0.546. The final length was 6.3 cm. and it was mounted as a compression specimen in the apparatus for direct measurement without magnification.

Two regular series of runs at 30° and 75° were made. The average departure of the 29 observed points from a straight line (no discards) was 0.15% and the mean departure from linearity was 4.9% of the maximum pressure effect. The departure from linearity was about 15% higher at the higher temperature than at the lower, a difference much beyond the limits of error. The final results are contained in the formulas:

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(86.92 - 97.5 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(89.72 - 107.3 \times 10^{-5}p)\,p.$$

The initial compressibility at 20° of lithium of density 0.534 was found by Richards to be 88×10^{-7}. This agrees with the above within the limits of error indicated by Richards' two significant figures.

Sodium. This was from Eimer and Amend, obtained before the war. It was not the identical lot, but was obtained at about the same time and is presumably similar to the lot for which I have already determined the effect of pressure on the electrical conductivity and melting point. No chemical analysis has been made, but the sharpness and high value of the freezing point are evidence of its high purity. The specimen was prepared by cutting from the interior of a large coherent block of sodium a smaller piece, perfectly clean and with no inclusions of any sort, and forming this by cold extrusion and pressing in a special mold into a cylinder 0.9 cm. in diameter and 2.5 cm. long. This was mounted as a compression specimen in the apparatus for direct measurement without magnification.

The two regular runs were made at 30° and 75°. There was no

incident at 30°; the points all lay smoothly and there was no perceptible permanent deformation after the run. At 75°, however, which is much nearer the melting point of this very soft substance, there was permanent set after the run, and it was obvious from the shape of the curve that the set had taken place during decreasing pressure, at the lower end of the pressure range. This set may easily have been due to viscosity in the transmitting medium. The last points at 75° were therefore discarded. Except for these points the mean departure of all the observed points from a smooth curve was 0.22%, and the maximum deviation from linearity 7.4% of the maximum pressure effect. The deviation from linearity was perceptibly greater at the higher temperature. Furthermore, the deviation is not symmetrical about the mean pressure, and it is not possible to represent the change of volume by a two constant formula in the pressure. In fact the deviation from linearity is so marked that I have thought it best to compute the changes of volume directly from the original data at every thousand kilogram interval at 30° and 75°. The values so computed are listed in the following table. The change of volume at each

TABLE II.

CHANGE OF VOLUME OF SODIUM UNDER PRESSURE.

Pressure kg/cm²	$\Delta V/V_0$ 30°	75°
1000	−.0153	−.0166
2000	.0299	.0321
3000	.0437	.0466
4000	.0570	.0602
5000	.0697	.0732
6000	.0819	.0856
7000	.0937	.0976
8000	.1050	.1093
9000	.1159	.1206
10000	.1263	.1316
11000	.1365	.1423
12000	.1465	.1528

temperature is computed in terms of the volume at atmospheric pressure and 20° (room temperature) as unity.

For comparison with the initial compressibility of Richards we may

either plot the above results on a large scale and draw the tangent to the curve at the origin, or we may pass a power series curve through the low pressure points. I have passed a three constant curve through the points at 1000, 2000, and 3000 kg. at 30° and obtain the formula:

$$\frac{\Delta V}{V_0} = -1.562 \times 10^{-5} p + 3 \times 10^{-10} p^2 + 1.6 \times 10^{-13} p^3.$$

This formula is not adapted to represent the change of volume outside its own range; already at 4000 kg. the change of volume given by the formula is 0.0566 against 0.0570 experimental. The above formula would give for the initial compressibility 156.2×10^{-7}. Richards' value for the average compressibility over the range of 500 kg. is 153×10^{-7}. He states that over his range the compressibility did not depart sensibly from constancy, but the above formula would show that the average compressibility over the range of 500 kg. differs from its initial value by 1.5×10^{-7}. Making this correction, the agreement with the result of Richards (now 154.5×10^{-7}) becomes closer, and perhaps is as good as could be expected.[25]

Potassium. This was from the same lot as that for which the effect of pressure on freezing point [15] and electrical conductivity [16] has already been determined. The high value and sharpness of the freezing point are evidence of its high purity. The material was prepared for these measurements by first filtering by forcing in a melted condition through a fine gauze under oil (Nujol); it was then cast under oil into a coherent slug, cleaned by scraping the outside surface, and finally formed by squeezing in a mold into a cylinder 0.9 cm. in diameter and 1.7 cm. long. This was mounted as a compression specimen in the apparatus for direct measurement without magnification.

A considerably more elaborate series of measurements was made on this than on other materials. I had already found [12] that the behavior of electrical resistance under pressure was unusual in that above 6000 kg. the temperature coefficient of resistance, which is usually constant over the entire pressure range, begins to decrease rapidly. At the time of making this observation I ventured the guess on theoretical grounds that at high pressures the thermal expansion would show a large rate of decrease. In order to determine the behavior of the thermal expansion at high pressures the following measurements were made. It is to be noticed that theoretically a measurement of the compressibility at two different temperatures is

capable of giving information as to the variation of thermal expansion with pressure, but the information so given is not very accurate. In the first place, the compressibility of potassium was measured in the ordinary way by two runs at 30° and 60°. The maximum pressure of these measurements was 10000 kg. instead of the usual 12000; the compressibility of potassium was so high that at 12000 kg. the relative deformation was beyond the range of the apparatus. At 60° the pressure was not allowed to fall below 500 kg., because of the proximity of the melting point. After these two series of runs over the pressure range, direct measurements of the thermal expansion were made by changing the temperature from 30° to 60° at constant position of the piston (constant mean pressure) at a number of different pressures distributed over the range. Two series of these temperature observations were made. The scheme of the method and the manner of computing the results is precisely the same as that which I have previously described in detail in connection with the measurement of the properties of liquids under pressure.[17] The only difference is that here the dimensions of the specimen are obtained by an electrical measurement instead of by measurement of the position of the piston. Is it not worth while again going into the details of the computations, which involve nothing not sufficiently obvious.

The average arithmetical departure from a smooth curve of the points of the two pressure runs (no discards) was 0.41% of the maximum pressure effect, and the average change corresponding to the thermal expansion under a 30° change of temperature was about ten times this. The measurements of thermal expansion, being much smaller, were not relatively so consistent among themselves. The first run for the determination of expansion gave scattering points at the high pressures, which, however, were not inconsistent with the later more accurate results. On the second run a better technique was used, and all the points except one lay on a smooth curve, this one lying off by some 25% of the observed effect. It is a question whether weight is to be attached to this discordant point. It has seemed to me that a certain amount of weight is to be attached to this point, as thus a curve is obtained without sudden changes of curvature, and the results tabulated have been thus computed. If no weight whatever is attached to this point, then the thermal expansion in the extreme case remains constant over the range from 6000 to 12000 kg., instead of dropping from 83 to 50, as shown.

The curvature of the graph of volume against pressure is so great that, as also in the case of sodium, it was necessary to compute the

changes of volume directly from the original data at intervals of 1000 kg. In the following table is given the changes of volume at even 1000 intervals at the mean temperature of 45°, obtained by taking

TABLE III.

VOLUME CHANGES OF POTASSIUM UNDER CHANGES OF PRESSURE AND TEMPERATURE.

Pressure kg/cm²	$\Delta V/V_0$ at 45°
1000	−.0330
2000	.0615
3000	.0867
4000	.1095
5000	.1306
6000	.1504
7000	.1694
8000	.1877
9000	.2053
10000	.2222
11000	.2385
12000	.2544
	Mean Thermal Expansion between 30° and 60°
0	.000241
2000	148
4000	105
6000	083
8000	073
10000	060
12000	050

the mean of the two series of measurements at 30° and 60°, and there is also shown the mean thermal expansion over this range, obtained by dividing the smoothed observed expansion over the range from 30° to 60° by 30. The tabulated changes of volume and the expansion are those of a mass of potassium that occupies 1 c.c. at 20° at atmospheric

pressure. The initial point of the thermal expansion curve was taken from the work of others; these measurements cannot give it.

To obtain the initial compressibility I have proceeded as in the case of sodium, passing a three constant power series in the pressure through the three lowest points. The formula so found is:

$$\frac{\Delta V}{V_0} = -3.565 \times 10^{-5} p + 2.85 \times 10^{-9} p^2 - 2 \times 10^{-13} p^3.$$

The formula is not good outside its range; at 4000 kg. it gives for ΔV 0.1098 against 0.1091 experimental, and at 10000 kg. 0.27 against 0.22 experimental. The formula shows that the initial compressibility at 45° is 356.5×10^{-7}, and the average compressibility over the range of 500 kg. 342.3×10^{-7}. The above values for the dependence of thermal expansion on pressure show that the temperature correction on this compressibility for reducing from 45° to 20° is 12.5×10^{-7}, making the average compressibility over the first 500 kg. at 20° 329.8×10^{-7}. The value given by Richards is 311×10^{-7}. Perhaps this is as good as could be expected in view of the experimental error and the range of the extrapolation above.

Especial attention is to be paid to the behavior of the thermal expansion under pressure, which is that anticipated theoretically. There can be no question of the large decrease; at the minimum, which is improbable, it has decreased by a factor of 3, and more probably by a factor of 5. The compressibility in the same range has decreased by a factor of 2. This reverses the initial behavior, for at low pressures the relative decrease of compressibility with pressure is about 50% greater than that of thermal expansion. The difference of behavior of metallic potassium and an ordinary liquid is of interest. Some time ago I measured the compressibility and expansion under pressure of a number of organic liquids.[13] The behavior of all these liquids is on the average roughly the same. The total change of volume under 12000 kg. of these liquids is about the same as for solid potassium, being 0.292 for the liquids against 0.254 for potassium. But the compressibility of the liquids shows a change which is relatively high, and is also much higher than the change of expansion. In the range of 12000 kg. the average compressibility of the liquids has changed by a factor of 15.2, whereas the expansion has changed by a factor of 4.66; potassium on the other hand has a considerably larger relative change in the expansion than in the compressibility. The significance of the behavior of potassium I believe to be that the outer shells of the atoms are being pushed tightly into permanent contact,

that the thermal agitation consists merely of a swinging back and forth within the atom of the heavy nucleus, and that the restoring force on the nucleus is proportional to a linear function of its displacement.

This completes the list of those substances which are known or presumed to crystallize in the cubic system, and for which therefore the assumption is justified that the linear compressibility is the same in all directions. Of the above list all except three have been definitely proved to be cubic. These three are Sr, Ur, and Tl. Sr resembles Ca chemically and is probably cubic. With regard to Ur there is not much basis for estimate. We have seen above that it is highly probable that Tl is not cubic because of the discrepancy between my value of the compressibility calculated above on the basis of uniform compressibility in all directions and that of Richards.

Metals Crystallizing not in the Cubic System.

No system except the cubic enjoys in general the property of having the same compressibility in all directions under hydrostatic pressure. It is, however, possible that there should be such relations between the elastic constants as to give this property to particular metals crystallizing in other systems, or it may be that the difference of compressibility in different directions is so small that experimentally it is not of importance. Now a study of crystal models makes it seem highly probable that in the hexagonal close packed arrangement of spheres the compressibility is the same in every direction. In fact the hexagonal and the cubic close packed arrangement of spheres are the same as far as the adjacent layers of atoms are concerned, so that any departure of the elastic properties of the hexagonal from that of the cubic close packed arrangements can be due only to forces between atoms separated from each other by at least one intervening atom, and these forces are presumably weak. Now of the metals studied here, magnesium crystallizes in the arrangement of hexagonally close packed spheres. (Of the metals listed above as cubic it will be found that Hull has evidence that two, cobalt and cerium, may also crystallize in the hexagonal system, but since the hexagonal arrangement in which these crystallize is the close packed arrangement of spheres, the compressibility would be expected to be the same in all directions, so that the possibility of the existence of two forms introduces no complications in the case of these two metals.)

It is probable therefore that the method of linear compressibility

gives at once without question the cubic compressibility of magnesium, and the data are accordingly given here.

Magnesium. This material I owe to the kindness of Professor C. C. Bidwell, who stated that it was of unusually high purity, but the exact chemical analysis was not known. Professor F. A. Saunders was kind enough to make a spectroscopic analysis for me with the following results: Fe, none, Zn, perhaps none, Ca small, Cu small, Al faintest trace, Sr none, Cd faintest trace.

The material was originally provided in the form of a square bar, about 1.3 cm. on a side and 1 cm. long. I extruded this in two stages at 500° to a piece of round section 0.3 cm. in diameter. It was straightened after extruding by rolling between iron plates heated to a dull red, and then annealed by heating for several hours to 300°, sealed in a glass tube to protect from oxidation. The final specimen, which was 8 cm. long, was placed in a steel sleeve in order to adapt it to the apparatus, and mounted as a compression specimen in the apparatus for direct measurement without magnification.

The regular series of runs at 30° and 75° was made. The average arithmetical deviation from a smooth curve of the 29 observed points (one discard) was 0.49% and the maximum deviation from linearity was 3.8% of the maximum pressure effect. The maximum deviation from linearity was the same at the two temperatures. Within the limits of error the deviation from linearity is symmetrical about the mean pressure so that it was possible to represent the results by a two constant formula.

In addition to the measurements on this pure sample, in the early stages of the development work several series of readings were made on an extruded sample of commercial magnesium of unknown purity obtained from Eimer and Amend. These results agreed within the limits of error, two or three per cent, with those found for the pure sample. This makes it probable that small impurities do not exert an important effect on the compressibility, and also lends much plausibility to the contention that the compressibility of this material is the same in different directions.

The final results are given by the formulas:

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(29.60 - 20.3 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(29.97 - 18.0 \times 10^{-5} p)\, p.$$

Richards gives for the average compressibility to 500 kg. (no distinction possible between the initial and the average compressibility) the value 29×10^{-7}, pressure being expressed in megabars. The correction for converting to kilograms would reduce this figure by about 2%. The formulas above give for the average compressibility to 500 kg. at 20° the value 29.4×10^{-7}. Considering the number of significant figures given by Richards, the agreement is within the possible experimental error, and thus we again have presumptive evidence of the equal compressibility of magnesium in all directions.

Magnesium is the only one of the non-cubic metals that may be expected to have equal compressibility in all directions. The other metals of this group measured were Bi, Sb, Cd, Sn, Zn, and Te. A complete description of their behavior would demand a determination of the compressibility in different directions specified with respect to the crystalline axes. This is much beyond the scope of the present work. For some of these metals the most that can be obtained from these measurements is some idea of the magnitude of the variation with direction that may be expected. This is given roughly by the variation in the numbers obtained for the compressibility with different methods of preparing the sample. The first strong evidence of this effect was found with bismuth.

Bismuth. The material used for these measurements was commercial electrolytic bismuth, obtained through the courtesy of the U. S. Lead Refinery, Inc. The properties of this bismuth have already been discussed in considerable detail [18]; the only measurable impurity is 0.03% of silver. Measurements were made on four samples. Two of these were castings, one cast in an iron mold, and the other in a thin walled graphite mold, chilled by slowly lowering into water. The other two specimens were extruded from the casting, the reduction in diameter being 2 to 1. Measurements on two of these samples, the casting in the iron mold, and one of the extruded pieces, were made with the preliminary apparatus, before the greatest accuracy was obtained. The initial compressibility at 30° of the extruded piece was 31.8×10^{-7}, and that of the casting 25.6×10^{-7}. The measurements of the casting were repeated to be sure that there was no error. Although these measurements were not as accurate as those finally made, still the accuracy was certainly one or two per cent, and the difference between these two samples was far beyond any possibility of experimental error.

Measurements on the two other samples, the casting made in graphite (density at 20° 9.803) and one of the extruded pieces (density

at 20° 9.797) were made with the finally perfected apparatus, that for direct measurement without magnification. The pieces were mounted as compression specimens, and their length was 16.3 cm. The mean deviation from a smooth curve of the 28 readings on the extruded specimen (no discards) was 0.32% of the maximum pressure effect, and the maximum departure from linearity was 3.5%. The corresponding figures for the casting (no discards) were 0.24% for the deviation from a smooth curve and 3.07% for the maximum departure from linearity. The final results are given by the formulas:

$$\text{Extruded cylinder, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(35.35 - 28.0 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(35.94 - 28.7 \times 10^{-5}p)\,p$$

$$\text{Cast cylinder, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(22.02 - 9.0 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(22.11 - 9.0 \times 10^{-5}p)\,p.$$

These results were calculated on the assumption of equal compressibility in all directions. One third the difference between the results is a minimum measure of the difference of the linear compressibility in different directions in the crystal. It is to be noticed that both the pressure coefficient and the temperature coefficients are greater in that direction in which the linear compressibility is the greater.

Richards and A. W. J. have both measured the cubic compressibility, that is, the mean of the linear compressibility in all directions. Richards finds for the initial value of bismuth of density 9.80, 29×10^{-7}. A. W. J. find the same initial value, and the average compressibility to 10000, corrected by my new value for iron, has dropped by 2.3×10^{-7} below its initial value. It is seen that both the initial value and the pressure coefficient of A. W. J. are included in the range of values above.

It should be possible to calculate the difference of the linear compressibility in different directions from the elastic constants of bismuth, but these do not seem to have been determined with sufficient accuracy.

Tin. The material was a melting point sample from the Bureau of Standards, and had the following analysis: Pb 0.007, Cu 0.003, Fe 0.002, Sb not detected, As and S trace, Sn (by diff.) 99.988. It was investigated in the form of a simple casting, cast in graphite and

annealed at a temperature of 150° for several hours after casting, of density 7.296 at 20°, or in the form of an extruded casting, the extrusion reducing the diameter from 1.2 cm. to 0.6 cm. The extrusion was performed at a temperature of about 125°, and after extrusion the piece was seasoned at 150° for several hours. The density of this piece at 20° was 7.302.

Two runs were made on the extruded pieces; one was with a preliminary form of apparatus and the results were not as accurate as those finally obtained. The preliminary run gave for the average compressibility to 12000 kg. at 30° 16.2×10^{-7}. The other run on the extruded piece was on a sample about 16 cm. long, mounted as a compression piece in the apparatus for direct measurement without magnification. The average arithmetical deviation from a smooth curve of the 40 readings (three discards) was 0.23% and the maximum deviation from linearity was 2.0% of the maximum pressure effect. The runs on the simple casting were also made in the final apparatus for direct measurement, and the specimen was also 16 cm. long. The mean arithmetical deviation from a smooth curve of the 28 readings (no discards) was 0.25%, and the maximum deviation from linearity was 1.09% of the maximum pressure effect. The values of cubic compressibility given by these two samples, assuming in the computation equal compressibility in all directions, was:

$$\text{Extruded rod, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(19.53 - 9.6 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(20.11 - 9.9 \times 10^{-5}p)\,p$$

$$\text{Cast rod, At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(17.01 - 5.17 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(17.37 - 5.75 \times 10^{-5}p)\,p.$$

The difference between extreme values is not as large as in the case of bismuth. Again the direction in which the linear compressibility is the greatest is the direction in which the pressure and the temperature coefficients of compressibility are the greatest. The crystal structure of ordinary tin determined by X-ray methods is side-face-centered tetragonal.

The initial compressibility at 20° of tin of density 7.29 is given by Richards as 19×10^{-7}. A. W. J. give 18.5 for the initial and 17.0 ×

10^{-7} (corrected for the new value of iron) as the average to 10000. The initial values of these two observers fall within the extremes above, but the decrease of compressibility with pressure found by A. W. J. is somewhat greater than the larger of the two above values.

Antimony. Two different specimens from two different sources were used. One was so-called chemically pure antimony from the J. T. Baker Chemical Co. It was cast in a graphite mold, the mold being preheated to above the melting point of antimony, and chilled by slowly lowering into water. The second specimen was antimony from Kahlbaum, his "K" grade. I have no analysis, but antimony from this source is known to be of high purity. This also was cast, but by pouring into a groove machined in a massive iron bar, the bar being cold. The manner of chilling the two castings was therefore entirely different, and the crystalline orientation in the two castings should be different. The casting of Baker's antimony, which was 14.6 cm. long, was mounted as a compression specimen in the apparatus for direct measurement without magnification. Its density at 20° was 6.678. The other casting, which was given its final shape by grinding, was 2.3 cm. long, and was mounted as a compression specimen in the lever apparatus for short specimens.

The regular series of runs at 30° and 75° was made on each specimen. The average arithmetical departure from a smooth curve of the readings on Baker's antimony (one discard) was 0.48%, and the maximum departure from linearity was 1.67% of the maximum pressure effect. For the casting of Kahlbaum's antimony the average arithmetical deviation from a smooth curve (four discards) was 0.68%, and the maximum deviation from linearity was 2.7%. The results, computed on the assumption of equal compressibility in all directions, are:

Baker's antimony, slowly cooled in graphite,

$$\text{At } 30° \quad \frac{V\Delta}{V_0} = -10^{-7}(14.69 - 6.2 \times 10^{-5}p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(14.80 - 6.3 \times 10^{-5}\,p)\,p\,.$$

Kahlbaum's antimony, rapidly chilled in iron,

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(20.41 - 12.9 \times 10^{-5}\,p)\,p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(20.50 - 12.9 \times 10^{-5}\,p)\,p\,.$$

The range of values is nearly as great as for bismuth. Here the temperature coefficient of compressibility is greater for that direction in which the linear compressibility is less, although the pressure coefficient of compressibility is less in this direction, as is to be expected.

For the initial value of the compressibility of antimony of density 6.71 Richards gives 24×10^{-7}. If there is no error, the significance of this result, when compared with that above, is merely that the two methods of casting adopted above did not bring out the extreme possible difference in the orientation of the crystalline grains.

Cadmium. Runs were made on three different samples. The first two were made from chemically pure cadmium from Eimer and Amend. The first was extruded at a temperature slightly below the melting point from a diameter of 1.2 to 0.6 cm., and was annealed at 230° for ten or fifteen minutes. Its density as 20° was 8.652. The second came from the same source and was cast in a graphite mold, preheated above the melting point, and the casting was cooled by lowering the mold slowly into water, and annealed after casting, as above. The density at 20° was 8.644. These two pieces were machined to a length of 16 cm. and mounted as compression specimens in the apparatus for direct measurement without magnification.

The source of the other specimen was Kahlbaum, his "K" grade. This is known to have only a few hundredths of per cent of impurity. This was cast in a special manner. The metal was melted in a tube of pyrex glass of diameter about 0.6 cm. in a cylindrical electric furnace mounted with its axis vertical. After temperature equilibrium was attained the glass tube was lowered slowly through the bottom of the furnace into the air of the room, thus allowing the metal in the lower part of the tube to solidify. The lowering was accomplished by clockwork, and was at the rate of about 12 cm. per hour. It will be seen that the conditions were highly favorable to a similar orientation of the crystals through the entire mass of the casting, except perhaps at the lower end where solidification began. It seems likely that in the long narrow tube, even if crystallization may originally begin about several nuclei, that eventually one surface of advance of the crystal, that on which growth is most rapid, will predominate over the others, and that after this, crystallization will consist merely in a single surface sweeping along the tube at a speed to keep pace with the lowering of the tube. This presumption as to the uniformity of crystal structure throughout the casting should be verifiable by X-ray analysis, or perhaps by a study of the etch figures; I have not yet made such an analysis. In the case of zinc and tellurium, which were cast in the

same way, the appearance of the casting indicated almost unescapably the similarity of the crystalline orientation throughout the mass. At any rate, this method of casting seems to offer important possibilities, and has at least brought out great differences in compressibility. A casting made in this way I shall call a "unicrystalline" casting.

Regular runs were made on the first two samples of cadmium at 30° and 75°; on the third a run only at 30° was made. The results with these castings of cadmium had as a rule more error than the other compressibility measurements; the irregularity is probably a real phenomenon, and may be due to a slipping of the crystalline grains under pressure. In one case the permanent deformation after the initial application of pressure was considerably greater than for most other metals.

For the simple casting of Eimer and Amend cadmium the average arithmetical departure from a smooth curve of the 27 observed points (no discards) was 0.29% and the maximum deviation from linearity was 2.28% of the maximum pressure effect. For the extruded casting of Eimer and Amend the arithmetical departure from smoothness (five discards) was 0.44% and the maximum deviation from linearity 2.33%. The unicrystalline casting of Kahlbaum's cadmium at 30° (one discard) gave the figures respectively 1.8% and 2.03%. The results calculated from these different specimens, assuming equal compressibility in all directions, are:

Eimer and Amend, simple casting,

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(19.54 - 10.7 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(20.19 - 11.0 \times 10^{-5} p)\, p\,.$$

Eimer and Amend, extruded casting,

$$\text{At } 30° \quad \frac{V\Delta}{V_0} = -10^{-7}(14.17 - 7.5 \times 10^{-5} p)\, p$$

$$\text{At } 75° \quad \frac{\Delta V}{V_0} = -10^{-7}(14.53 - 7.7 \times 10^{-5} p)\, p\,.$$

Kahlbaum's, unicrystalline casting,

$$\text{At } 30° \quad \frac{\Delta V}{V_0} = -10^{-7}(8.57 - 3.8 \times 10^{-5} p)\, p\,.$$

The range in values is very striking, being almost two and a half fold. The difference between the figures for the ordinary and the unicrystalline casting tends to be the extreme. This is as one would expect, because the manner of chilling would tend to make that surface which grows along the axis of the unicrystalline cylinder grow at right angles to the exterior curved surface in the simple casting, advancing along the radius.

The initial compressibility at 20° of cadmium of density 8.60 was found by Richards to be 21×10^{-7}. A. W. J. found for the initial compressibility 22.2×10^{-7}, and for the average compressibility to 10000, 19.2×10^{-7}. This pressure coefficient of compressibility is at the extreme edge of the values found above, but the initial compressibility of these two observers is outside the range above, which would mean a greater variation of compressibility with direction than is suggested by my measurements.

Zinc. All the specimens were made from melting point samples of the Bureau of Standards of the following analysis: Pb 0.0026, Cd 0.0022, Fe 0.0034, Cu (not detected), Zn (by diff.) 99.992. More elaborate measurements were made on this than on any other metal, and the results show a greater effect of crystal structure. In general the results were much more irregular than for any other metal; there were more likely to be permanent distortions after the first application of pressure, there was quite often hysteresis, and the relation between pressure and deformation did not depart regularly from linearity, but on several occasions curves were found with distinct points of inflection. (The total departure from linearity of these abnormal cases was never large.) It will not pay to describe in detail all the anomalous effects found, but I will give merely the average compressibility between 0 and 12000 kg. at 30°. The effect of temperature was studied in only one or two cases.

With the preliminary apparatus measurements were made on three different samples. The first of these, a casting, had an average compressibility between 0 and 12000 kg. of 24×10^{-7}, the second, an extruded casting, had a mean compressibility of 12.8×10^{-7}, and the mean compressibility of the third, also an extruded casting, was 10.7×10^{-7}. Measurements with the final form of apparatus and another simple casting gave for the mean compressibility 9.04×10^{-7}, and on an extruded casting 8.58×10^{-7}. The density at 20° of the simple casting was 7.129, and of the extruded casting 7.134.

Finally a unicrystalline casting was made by the procedure described under cadmium, and measurements made of the compressibility of

this in three mutual perpendicular directions. This was accomplished as follows. First the casting in its original form, 16 cm. long, was measured in the regular way as a compression specimen. From this casting were then cut four cubes 0.6 cm. on a side, marking the orientation with respect to the original casting, and these cubes were piled on top of each other, and the linear compressibility measured along the axis of the pile for two different ways of piling the cubes together, corresponding to two directions at right angles to the axis of the original casting. These measurements were made in the lever apparatus for long specimens. The mechanical properties of this casting were quite unusual in that it was very flexible, so that great difficulty was experienced during the machining of the cubes to prevent the casting from bending. The bending was not accompanied by the characteristic noise of the bending of an ordinary casting. It seems not unlikely that the stiffness of the ordinary zinc casting is due to a dovetailing together of crystal grains in different orientations, which cannot be deformed as a single homogeneous mass because of the great difference of the elastic constants of the grains in different directions.

Dr. G. L. Clark has been so kind as to make an X-ray analysis of this specimen of zinc for me, and finds, within the possible errors of the method, that the crystalline orientation is indeed the same throughout the specimen, and furthermore that the direction of the hexagonal axis is along the axis of the original casting within a few degrees.

The results found for the cubic compressibility of the unicrystalline casting in three mutually perpendicular directions, (that is, the linear compressibility in these directions multiplied by three) were: along the axis of the original casting 4.98×10^{-7}, one of the perpendicular directions, 15.9×10^{-7}, and the other perpendicular direction 21.4×10^{-7}. The average of these three is 14.1×10^{-7}, which is approximately the average cubical compressibility, and would be the result of a single measurement by the method of Richards or A. W. J. The initial value of Richards is 17×10^{-7}. The initial value of A. W. J. is 17.1×10^{-7}, and their average value to 12000, corrected according to the new values for iron, is 15.1×10^{-7}. The agreement of this last figure with the average above is as close as could be expected when one considers the possible error of my measurements on four small cubes piled together, and constitutes very strong evidence as to the reality of the large differences of linear compressibility found above in different directions.

Tellurium. This material I owe to the kindness of the Raritan Copper Works, from whom I obtained it a number of years ago. I

have no chemical analysis. This was prepared as a unicrystalline casting in the manner already described for cadmium. The crystalline figures were very prominent in this casting, and show the orientation of the crystal to be the same throughout the entire casting. The appearance of the casting is somewhat tree-like, the axis of the tree is inclined at an angle of about 15° to the axis of the casting.

The specimen was mounted as a compression specimen (length 16 cm.) in the apparatus for direct measurement. Only a few measurements were made on it, because it was at once evident that the behavior is such as to be worthy of much more detailed study, which must be put off until a systematic investigation can be made of the variation of compressibility with direction of a large number of crystals. The measurements, as far as they went, were perfectly regular. There was very little permanent set on the first application of pressure, and the relation between distortion and pressure was sensibly linear. The startling result found for this substance was that its compressibility along the axis of the casting is negative; that is, that it lengthens along the axis when subjected to a uniform hydrostatic pressure all over. Its average *linear* compressibility in this direction was -2.36×10^{-7}.

Paradoxical as this behavior appears, there is nothing inherently impossible about it, and something analogous has been observed by Voigt in the negative Poisson's ratio in certain directions in pyrites. (This remark is merely by way of analogy; the linear compressibility of pyrites is not negative in any direction.)

Discussion of Results.

Although the experiments just described give the compressibility of some substances not measured before, and also I believe give the compressibilities with greater accuracy than hitherto attained, the principle interest in the measurements is in the variations of compressibility with temperature and pressure. The variation of thermal expansion with pressure is also given by the experiments, because of course it is a mathematical identity that the pressure coefficient of thermal expansion is the same as the temperature coefficient of compressibility.

The results of these experiments are collected in Table IV. In the first column is given the name and description of the substance, in the second column the initial compressibility at 30° multiplied by 10^7,

TABLE IV.

Collected Results.

Substance	χ_0 at 30° $\times 10^7$	$\left(\frac{1}{\chi}\frac{\partial\chi}{\partial p}\right)_0 \times 10^6$	$-\left(\frac{1}{\alpha}\frac{\partial\alpha}{\partial p}\right)_0 \times 10^6$	$\frac{-1}{\chi_0}\left(\frac{1}{\alpha}\frac{\partial\alpha}{\partial p}\right)_0$	$\left(\frac{1}{\chi^2}\frac{\partial\chi}{\partial p}\right)_0$
Al, hard drawn	13.40	.52	....	....	3.90
drawn and annealed	13.34	.50	1.76	13.2	3.96
cast	13.43	.74	1.02	7.6	5.70
Sb, Kahlbaum's cast	20.41	1.26	0.61	3.0	6.2
Baker's cast	14.69	.84	0.75	5.13	5.74
Bi, cast	22.02	.82	0.50	2.27	3.92
extruded	35.35	1.58	3.3	9.30	4.50
Cd, Eimer and Amend extruded	14.17	1.06	1.08	7.64	7.48
Eimer and Amend cast	19.54	1.10	1.89	9.67	5.60
Kahlbaum's unicrystalline	8.57	.88	....	....	10.32
Ca, G. E. Co.	59.46	1.64	.62	1.04	2.76
Prof. Bidwell's	56.97	1.66	4.5	7.90	2.90
Ce, extruded	35.74	1.06	....	....	2.98
Co, wire	5.39	.78	.48	8.93	14.28
Cu, Bureau of Standards	7.19	.72	.67	9.35	10.06
commercial, unannealed	7.32	.74	.31	4.23	10.06
commercial, annealed	7.29	.74	.36	4.94	10.06
Ge, casting	13.78	.98	....	....	7.16
Au, short specimen	5.78	.74	....	....	
long specimen	5.77	1.08	....	....	18.66
Fe, pure	5.87	.70	.37	6.30	12.16
Pb, cast	23.73	1.46	1.51	6.35	6.14
extruded	23.05	1.04	1.46	6.32	4.64
Li, extruded	86.92	2.24	3.3	3.8	2.58
Mg, extruded	29.60	1.36	1.05	3.54	4.64
Mo, drawn wire	3.61	.58	.2	5.54	16.12
swaged rod	3.47	.72	.2	5.76	20.8
Nichrome, wire	5.50	.54	....	....	9.94
Ni, commercial rod	5.25	.80	.16	3.04	15.2
pure wire	5.29	.80	.32	6.05	15.0
Pd, drawn rod	5.19	.80	....	....	15.54
drawn wire	5.28	.80	.18	3.41	15.02
Pt, drawn rod	3.05	.0	.33	10.8	.0
drawn wire	3.60	1.00	.33	9.2	28.0
K,	356.5	23.	20.	5.62	9.76
Ag, drawn rod	9.87	.90	.66	6.68	9.04
Na,	156.2	7.8	.37	4.43	4.92
Sr, extruded	81.87	1.78	....	....	2.16
Ta, wire	4.79	.10	1.26	2.63	2.18
Sn, extruded	19.53	.98	1.92	9.85	5.04
cast	17.01	.60	1.19	7.00	3.58
W, drawn wire	3.15	1.02	.2	1.24	32.2
swaged rod	2.93	1.02	.4	13.7	35.0
Te, unicrystalline casting	−7.1	....	....	....	....
Tl, extruded	34.2	3.36	1.53	4.48	1.94
Ur, rolled sheet	9.66	.52	....	....	5.36

(this is merely the coefficient "a" of the formula $\frac{\Delta V}{V_0} = -ap + bp^2$, where p is expressed in kg/cm²). In the third column is given the initial proportional change of compressibility with pressure, or $\left(\frac{1}{\chi}\frac{\partial \chi}{\partial p}\right)_0$. Here $\frac{\partial \chi}{\partial p}$ is $2b$ of the above formula for change of volume, and χ_0 is the "a" of the formula. In the fourth column is given the initial proportional change of thermal expansion with pressure $\left(\frac{1}{\alpha}\frac{\partial \alpha}{\partial p}\right)_0$. In calculating the figures of this column, the derivative $\left(\frac{\partial \alpha}{\partial p}\right)_0$, which is the same as $\left(\frac{\partial \chi}{\partial t}\right)_0$ or $\frac{\partial a}{\partial t}$, was computed from the detailed formulas already given for the compressibility at 30° and 75° merely by subtracting the value of "a" at 30° from the value at 75° and dividing by 45. The value of α_0 I took in most cases from the table in the paper of Richards [1] summarizing his compressibility data. In the fifth column is given the proportional change of expansion of the fourth column divided by the compressibility "a." Finally in the sixth column is given the proportional change of compressibility divided by the compressibility. An examination of the details of the measurements will show that less accuracy is to be attached to quantities involving changes with temperature than with pressure.

In every case the compressibility decreases with increasing pressure. This is entirely what we would expect, but I do not know that there is any necessity here, so that a case of increasing compressibility with pressure would violate any of the laws of physics. In fact it is not at all inconceivable that this may be found to be actually the case for some exceptional substances. For instance, there are a number of cases known in which the polymorphic form with the smaller volume has the larger compressibility, and it is conceivable that a change similar to one which in the case of polymorphism takes place abruptly might in some cases be brought about gradually by increasing pressure, so that the form stable at the higher pressures and therefore with the smaller volume should be the more compressible. In fact for potassium the proportional compressibility, $\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau$, does increase slightly at the higher pressures.

The order of magnitude of the change of compressibility with pressure, when pressure is expressed as here in terms of kilograms per

square centimeter, is seen to be 10^{-5}. The dimensions of this number are those of the reciprocal of a pressure.

The thermal expansion also decreases numerically with increasing pressure in nearly all the cases above, but there are at least two substances in the list above which give a negative change of thermal expansion with pressure that seems to be beyond the experimental error. These are germanium and uranium. Unfortunately the expansion at atmospheric pressure of these substances does not seem to have been determined, so that the proportional change could not be computed, and blanks were accordingly left in the third column of Table IV. The other blanks in this column are also due to missing data, either my own, or that of expansion at atmospheric pressure. Again the order of magnitude of the change of expansion with pressure is 10^{-5}.

The physical significance of the fifth and sixth columns is easy to see. We may write $\frac{1}{\chi^2}\frac{\partial \chi}{\partial p}$ as $\frac{1}{\chi}\left(\frac{1}{\chi}\frac{\partial \chi}{\partial p}\right)$. Now the dimensions of $1/\chi$ are those of a pressure, and numerically $1/\chi$ is the pressure required to halve the volume. Hence $\frac{1}{\chi^2}\frac{\partial \chi}{\partial p}$ is the proportional change of compressibility under a pressure that would halve the volume. Similarly $\frac{1}{\chi}\frac{1}{\alpha}\frac{\partial \alpha}{\partial p}$ is the proportional change of thermal expansion under a pressure which would halve the volume. Both of these quantities are dimensionless, and the most immediately interesting thing about them is their order of magnitude, which is that of a small number. That this would be found to be the case was anticipated some years ago by the theory of the solid state of Grüneisen.[19] Grüneisen's theory went farther, and gave an exact expression for this number in terms of the exponents in the assumed law of attraction and repulsion between the atoms. This exact expression does not seem, however, to fit at all well, and it is most doubtful whether the details of Grüneisen's theory can be maintained. The fact that these two ratios are of the order of magnitude of a small number would probably be given by a number of simple theories, simply because they are dimensionless.

The relative magnitude of the changes of compressibility and expansion with pressure is of some interest. The considerations which I have already mentioned in the case of potassium would lead one to expect that at very high pressures the thermal expansion becomes vanishingly small. But if one plots the above values, ruling out those metals which do not crystallize in the cubic system, it will be found

that there are only three, Al, Pb, and Li, for which the thermal expansion initially decreases more rapidly than the compressibility. Even potassium is in the list of those whose compressibility at first decreases more rapidly than the expansion. But at high pressures we have seen that this state of affairs is reversed in the case of potassium. Computation will show that this is also the case for sodium, the expansion at 12000 kg. having dropped to about one third of its initial value, while the compressibility has dropped to two thirds. This may well be the behavior of all metals at sufficiently high pressures.

Theoretical Considerations.

By far the most successful theoretical attempt to account numerically for the compressibility of solid substances is that which Born [3] has developed and applied to crystals of the type of NaCl and also to CaF_2 and ZnS. The fundamental thesis of this theory is that the solid is maintained by electrostatic forces, there being in the position of the center of each chlorine atom, in NaCl for example, a single elementary negative charge, and at the center of the Na atom a single elementary positive charge. In addition to the forces between the charged ions, which act on each other according to the inverse square law, there are also mutual repulsions between adjacent atoms due to the electrons in the outer shells of the atoms. Equilibrium is due to a balance between the attractive and repulsive forces. It should be possible to calculate the repulsive forces as well as the attractive forces if the distribution of the electrons within the atom is known. From the assumption that the electrons are in cubical array in the interior of the atom, as they are supposed to be from other considerations, Born has deduced that the potential of the repulsive forces is as the inverse ninth power of the distance between atomic centers, and has furthermore shown that the inverse ninth power gives numerically very approximately the compressibility of crystals of the type of NaCl.

Naturally the first inquiry of an attempt to extend this theory to include metals is whether the fundamental thesis still holds, namely that the forces are essentially electrostatic in nature and are due to single elementary charges or small integral multiples of them situated at the centers of the atoms. A dimensional argument as to the order of magnitude of the quantities involved suggests that the same fundamental thesis does indeed hold. A quantity of the dimensions of compressibility ($M^{-1} LT^{-2}$) is to be built up from the electronic

charge e (dimensions of e^2 are MLT^{-2}) and δ, the distance of separation of atomic centers (L). The required combination is at once found to be δ^4/e^2. The very fact that it is possible to build up a combination of these two quantities of the right dimensions is presumptive evidence of the correctness of our general considerations, because in general it would require three (instead of two) quantities to give in combination the dimensions of any one arbitrarily given quantity. This dimensional argument suggests, therefore, that compressibility should be of the order of magnitude of δ^4/e^2. Now assuming simple cubic structure, and expressing δ in terms of the quantities in terms of which it is determined in practise, that is in terms of atmoic weight, density, and the mass of the hydrogen atom, we find that the compressibility is of the order of magnitude of $\frac{(\text{Mass of H atom})^{\frac{4}{3}}}{e^2} \times \left(\frac{\text{At. Wt.}}{\text{Density}}\right)^{\frac{4}{3}}$, or substituting numerical values for e and the mass of the hydrogen atom,

$$\text{Compressibility is of order of } 8.6 \times 10^{-14} \left(\frac{\text{At. Wt.}}{\text{Density}}\right)^{\frac{4}{3}}.$$

Here of course, compressibility is in absolute units, that is, the unit of pressure is 1 dyne/cm^2.

In table V is given the compressibility in absolute units divided by $10^{-14}\left(\frac{\text{At. Wt.}}{\text{Density}}\right)^{\frac{4}{3}}$, for most of the metals measured above. It is seen that the numbers are of the order of magnitude of 8.6, as our argument suggests.

Although the argument is crude, it seems to me that the result is of great significance, because it suggests that in the metal, as well as in salts, the atoms become charged by losing valence electrons, and the metallic structure is held together by the forces between positively charged residues of the atoms and the lost electrons. It is furthermore to be presumed that the lost electrons take some definite position in the crystal lattice, as for instance, the measurements of Hull [20] make so probable in the case of calcium.

To make the next step in refinement in the computation, we must take account of the exact arrangement of the atoms in the lattice, and must also know the law of repulsion. As far as the arrangement of the atoms in the crystal structure goes, the results of X-ray analysis indicate very definitely in at least some cases what we must expect. Thus Hull [20] has found in the case of metallic calcium that the Ca atoms have exactly the same arrangement as the Ca atoms in CaF_2.

TABLE V.

COMPARISON OF COMPRESSIBILITY WITH THE ORDER OF MAGNITUDE SUGGESTED BY DIMENSIONAL ANALYSIS.

Metal	Compress $10^{-14}\left(\frac{\text{At Wt.}}{\text{Density}}\right)^{\frac{4}{3}}$
Li	27.5
Na	23.0
K	22.1
Ca	7.43
Sr	7.30
Mg	8.8
Zn	7.8
Cd	6.7
Cu	5.2
Ag	4.4
Au	2.6
Ge	4.4
Sn	4.6
Pb	4.8
Sb	5.05
Bi	5.10
Mo	1.72
W	1.48
U	3.26
Fe	4.4
Ni	4.3
Co	4.1
Pd	2.7
Pt	1.9

The inference is strongly suggested that in metallic Ca the electrons take the place of the F atoms in CaF_2, and if this is the case, it should be possible to take over with slight modification the considerations

which Born has applied to calculating the compressibility of CaF_2. There is also another group of metals about which we may make very plausible assumptions about the positions of the electrons in the lattice. The Na atoms by themselves or the Cl atoms by themselves form in NaCl a face centered cubic lattice. Hence it is natural to expect that the complete crystal structure (meaning by this the arrangement of ions and free electrons) of those metals which are univalent, and therefore readily lose a single electron, and whose atomic nuclei have been proved to crystallize face centered cubic, should be exactly like that of NaCl. Several of the metals of the above list are in this class: Cu, Ag, Au, and probably Pb.

In addition to the crystal structure, we must also know the law of repulsion. This is a much more uncertain matter. An uncritical extension of the argument given by Born would indicate a repulsion whose potential is as the inverse fifth power of the distance of separation of ions and electrons, since his first term in his fundamental development for the potential of a neutral cube and a single point charge is the inverse fifth. A more critical examination of this discussion will raise several doubts, however, and in fact it is very questionable to me how much significance is to be given to the inverse ninth power which Born deduces for NaCl. It is in the first place disconcerting to discover that the inverse fifth power term for a compound lattice of electrons and ions has the wrong sign, so that instead of a repulsion we have an attraction. However, in computing what the action is between a neutral cube and an electron there are several matters with regard to which we are in serious doubt and which may greatly affect the result. Thus the statement that the force between an ion and an external electron is of the wrong sign is based on the assumption that the electron is situated on one of the three axes of the cube perpendicular to the faces at their mid-points. This corresponds to the arrangement assumed by Born for the cubical atoms in NaCl. But it is evident that if the electron approaches the neutral cube along a diagonal, the force will be of repulsion instead of attraction. In crystals not of the simple type of NaCl it is not at all obvious what the arrangement of the cubical atoms in the crystal lattice is, for the symmetry of the crystal does not seem to be consistent with the cubical symmetry of the atom. Thus in the case of CaF_2, the Ca atom is surrounded by 12 other atoms symmetrically situated, so that the symmetry of the dodecahedron is indicated.

Even if the orientation of the atoms with respect to the electron is known and is that assumed by Born, still the inverse fifth power must

be open to grave question. Born developed the potential of the cube at external points in a power series, of which the first term was the inverse fifth, the development being good at points whose distance from the center of the cube is large compared with the semi-diagonal, or in other words, the dimensions of the atom are assumed small in comparison with their distances apart. Now this is almost certainly not the case, but a number of lines of argument indicate that the atoms pretty completely fill the total space, and that their external shells are nearly in contact. Hence in most of the cases in practise we can certainly say that more terms than the first of the series are necessary to give an adequate representation, and that probably under many actual conditions the series is actually divergent.

There is another important consideration with regard to the series development. In computing the compressibility it is necessary to differentiate the expression for the potential. Now although the numerical magnitude of the potential itself may perhaps be given with sufficient approximation by the first term of the series, it is quite another matter to expect the derivative to be given by the derivative of the first term.

Apart from these considerations, which after all are concerned with the method of computing the results, there is still another consideration which reaches deeper, and involves the physical picture back of the computations. This has been suggested by Schottky [21] in a recent paper. He finds quite general theorems for electromagnetic systems like the system of ions and electrons in a crystal which connect the changes of internal kinetic and potential energy of the system with the external forces acting on the system. In particular, for a system under external hydrostatic pressure, Schottky obtains the result,

$$\begin{aligned} d\bar{L} &= -\ d\bar{U} + 3d\,(pV) \\ d\bar{E} &= \ \ 2d\bar{U} - 3d\,(pV), \end{aligned}$$

where L is the internal kinetic energy, E the internal electro-magnetic energy, and U the total energy of the system. The dashes indicate average values over a time sufficiently long for the average values to be constant. If in particular we now subject the system to an isothermal change of pressure, we have by thermodynamics

$$d\bar{U} = -\left\{\tau\left(\frac{\partial v}{\partial \tau}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_\tau\right\} dp.$$

Substituting above,

$$d\overline{L} = \left\{ 3v + \tau \left(\frac{\partial v}{\partial \tau}\right)_p + 4p \left(\frac{\partial v}{\partial p}\right)_\tau \right\} dp.$$

Now in a solid under normal conditions we may suppose the kinetic energy of motion of centers of mass of the atoms to be a function of temperature only, so that at constant temperature this part of L is constant. But the equation above gives at moderate pressures an increase of L with pressure. As Schottky points out, this means an increase of internal kinetic energy of rotation of the electrons in the atoms about the nuclei, which again means a decrease of atomic radius. In other words, the atoms shrink in size as pressure increases. This reminds one strongly of the compressible atom of Richards.[22] What is more, the change of size is very considerable, so that when a substance is compressed the force between the atoms changes for two reasons, both of the same order of magnitude, one reason being the change in the distance between atomic centers, and the other the change in the dimensions of the atom. This will evidently introduce another term into Born's equation, and will essentially modify his results. The modified analysis is perhaps worth giving. While we are giving the analysis, we may as well carry the work one step further than Born has in his published papers, because we can thereby get the variation of compressibility with pressure.

If the atom is deformable, the coefficient of the repulsive force can no longer be regarded as a constant, but will depend on the distance of separation of the atoms. Born's analysis for the forces exerted by a cube suggests that this coefficient is proportional to the fourth power of the atomic radius.

We assume as the starting point, as does Born, that the potential energy per unit cell of the lattice is of the form

$$\Phi = -\frac{a}{\delta} + \frac{b}{\delta^n}.$$

δ is the lattice constant, and may be computed in terms of the lattice structure and its elementary charges. The coefficient b should be directly computable in terms of the details of the structure, but it must also satisfy a condition imposed by the stability of the lattice. n should also be computable in terms of the details of the structure, but again may also be found in another way, namely, from the compressibility. Thus we have here the possibility of two checks, one on n and

one on b. Born has availed himself only of the check on n given by compressibility measurements.

All the following considerations take no account of temperature; they hold rigorously at absolute zero, but approximately at higher temperatures, because compressibility does not greatly depend on temperature.

Given a structure with a potential, like the above, and subjected to external pressure, then a necessary condition of equilibrium in general is that

$$\Phi + p\delta^3$$

shall be a minimum for changes of δ, or

$$\frac{d\Phi}{d\delta} + 3p\delta^2 = 0.$$

In particular, when there is no external pressure, and $\delta = \delta_0$,

$$\left.\frac{d\Phi}{d\delta}\right|_{\delta=\delta_0} = 0.$$

The compressibility we define in accordance with the experimental usage above as

$$\chi = \frac{1}{\delta_0{}^3}\frac{d\delta^3}{dp} = \frac{3\delta^2}{\delta_0{}^3}\frac{d\delta}{dp}.$$

We can get $\frac{d\delta}{dp}$ by differentiating the equation of stability, which is, solved for p,

$$p = -\frac{1}{3\delta^2}\frac{d\Phi}{d\delta}.$$

Hence

$$\frac{dp}{d\delta} = \frac{2}{3\delta^3}\frac{d\Phi}{d\delta} - \frac{1}{3\delta^2}\frac{d^2\Phi}{d\delta^2}.$$

We must next evaluate the derivatives of Φ.

$$\frac{d\Phi}{d\delta} = \frac{a}{\delta^2} - \frac{nb}{\delta^{n+1}} + \frac{1}{\delta^n}\frac{db}{d\delta},$$

$$\frac{d^2\Phi}{d\delta^2} = -\frac{2a}{\delta^3} + \frac{n(n+1)b}{\delta^{n+2}} - \frac{2n}{\delta^{n+1}}\frac{db}{d\delta} + \frac{1}{\delta^n}\frac{d^2b}{d\delta^2}.$$

With regard to b as a function of δ, we shall content ourselves with the next order of approximation beyond assuming that it is constant, and put

$$b = \alpha + \beta\delta .$$

Substituting this value back,

$$\frac{d\Phi}{d\delta} = \frac{a}{\delta^2} - \frac{n(\alpha+\beta\delta)}{\delta^{n+1}} + \frac{\beta}{\delta^n}$$

$$\frac{d^2\Phi}{d\delta^2} = -\frac{2a}{\delta^3} + \frac{n(n+1)}{\delta^{n+2}}(\alpha+\beta\delta) - \frac{2n}{\delta^{n+1}}\beta ,$$

and the special value of $\frac{d\Phi}{d\delta}$ at $\delta = \delta_0$ gives

$$\frac{a}{\delta_0^2} - \frac{n(\alpha+\beta\delta_0)}{\delta_0^{n+1}} + \frac{\beta}{\delta_0^n} = 0 .$$

Now substitute these values for the derivatives of Φ, and we get

$$\frac{dp}{d\delta} = \frac{4a}{3\delta^5} - \frac{n(n+3)}{3\delta^{n+4}}\alpha - \frac{(n+2)(n-1)}{3\delta^{n+3}}\beta ,$$

$$\chi = \frac{3\delta^2}{\delta_0^3} - \frac{3\delta^5}{4a - \frac{n(n+3)}{\delta^{n-1}}\alpha - \frac{(n+2)(n-1)}{\delta^{n-2}}\beta} .$$

In this equation replace α in terms of δ_0 by the stability relation, put $\delta = \delta_0 + \Delta\delta_0$, where $\Delta\delta_0$ is small, so that

$$\left(\frac{\delta_0}{\delta}\right)^{n-1} = 1 - (n-1)\frac{\Delta\delta_0}{\delta_0} ,$$

$$\frac{1}{\delta^{n-1}} = \frac{1}{\delta_0^{n-1}}\left[1 - (n-1)\frac{\Delta\delta_0}{\delta_0}\right] ,$$

and

$$\frac{1}{\delta^{n-2}} = \frac{1}{\delta_0^{n-2}}\left[1 - (n-2)\frac{\Delta\delta_0}{\delta_0}\right] ,$$

replace $\frac{\Delta\delta_0}{\delta_0}$ by $\frac{1}{3}\frac{\Delta V}{V_0}$, and substitute back, obtaining

$$\chi = \frac{-9\delta_0^4}{(n-1)\left(a - \frac{\beta}{\delta_0^{n-2}}\right)} \left\{ 1 + \tfrac{1}{3} \left\{ 7 + \frac{a(n+3) - \frac{2n+1}{\delta_0^{n-2}}\beta}{a - \frac{\beta}{\delta_0^{n-2}}} \right\} \frac{\Delta V}{V_0} \right\}.$$

The initial compressibility $\left(\frac{\Delta V}{V_0} = 0\right)$ is therefore,

$$\chi_0 = \frac{-9\,\delta_0^4}{(n-1)\left(a - \frac{\beta}{\delta_0^{n-2}}\right)}.$$

This agrees with Born's expression on putting $\beta = 0$.

Now apply this formula to numerical computation. What we are interested in is the order of magnitude of β, to see whether it checks with what might be expected by Schottky's theorem. We apply the formula to calcium. For this metal the evidence is particularly strong that we are dealing with a space lattice of doubly charged positive ions and electrons, the ions occupying the position of Ca in CaF_2, and the electrons the position of F. Born has worked out the analysis for this type of lattice, so that we may apply his results directly. We have numerically

$$\begin{aligned} a &= 38.7e^2 = 8.78 \times 10^{-18}, \\ \delta_0 &= 5.56 \times 10^{-8}, \\ \chi_0 &= -5.7 \times 10^{-12}. \end{aligned}$$

Let us assume at first that $\beta = 0$. Then solving for n, we find

$$n = 2.72,$$

which is much lower than the 5 suggested by Born's analysis for neutral cubes and electrons.

Let us now assume $n = 5$, and see what this gives for β.

$$\beta = \delta_0^3\left(a + \frac{9\delta_0^4}{4\chi_0}\right)$$

$$= 8.5 \times 10^{-40}$$

Now let us see what Schottky's theorem would lead us to expect for the order of magnitude of β. We have

$$\beta = \frac{db}{d\delta} = \frac{db}{dp}\frac{dp}{d\delta}$$

$$\frac{d\delta}{dp} = \frac{\delta\chi}{3}.$$

Hence

$$\beta = \frac{3}{\chi\delta}\frac{db}{dp}$$

Now the analysis of Born (equation 4, page 235, Verh. D. Phys. Ges. 20, 1918) shows that b is of the form

$$b = \text{Const } e^2 r^4,$$

where r is the semidiagonal of the neutral cubic atom, and the constant, which varies with the type of lattice, will be of the order of magnitude of 10. (For instance, the coefficient of e^2 in the above expression for a is 38.7, for NaCl it is 13.94). Hence as a rough approximation put

$$b = 10\, e^2 r^4,$$

and

$$\frac{db}{dp} = 40 e^2 r^3 \frac{dr}{dp}.$$

Now Schottky's theorem gives $\frac{dr}{dp}$. At ordinary temperatures, at low pressures, his formula gives very closely

$$\frac{dL}{dp} = 3V,$$

and hence, applied to an elementary cell of the lattice,

$$\frac{dL}{dp} = 3\delta^3 = \frac{dL}{dr}\cdot\frac{dr}{dp}.$$

Now the variable part of L we take as the contribution of the 8 outer electrons rotating about a nuclear charge of 8 at distance r. (This assumes most of the deformation of the atom under pressure is confined to the outer shell). The kinetic energy of these electrons is one half their potential energy, or

$$L = \frac{32\,e^2}{r},$$

$$\frac{dL}{dr} = -\frac{64\,e^2}{r^2},$$

$$\frac{dr}{dp} = -\frac{3\delta^3 r^2}{64\,e^2},$$

$$\frac{db}{dp} = -\frac{15}{8}\delta^3 r^5,$$

and finally,

$$\beta = -\frac{45}{8}\frac{\delta^2 r^5}{\chi}.$$

To find r, we assume that one side of the cubic atom is $\frac{2}{3}\,\delta$,

or $$r = \frac{\delta_0}{\sqrt{3}} = 0.577\,\delta_0.$$

Hence, substituting numerical values

$$\beta = +\,1.04 \times 10^{-40}.$$

Now this is of the same sign, and of the same order of magnitude as the value required experimentally to make a plausible change in the value of n. When we are dealing with exponents as high as 40, it would seem that an agreement of order of magnitudes is of considerable significance. Hence we conclude that the Schottky effect must certainly be expected to play an important part (a conclusion also stated by Schottky, although without numerical computation). Consideration of the effect makes the value of n required to give the right compressibility larger than it otherwise would be.

The conclusion to be drawn from all these considerations I believe to be that we are not yet in a position to attach much significance to the precise value of n necessary to give the best value of compressibility.

An interesting suggestion as to the compressibility of solids at extremely high pressures is contained in Schottky's equation

$$\left(\frac{\partial \overline{L}}{\partial p}\right)_\tau = 3v + \tau\left(\frac{\partial v}{\partial \tau}\right)_p + 4p\left(\frac{\partial v}{\partial p}\right)_\tau.$$

The term $\tau\left(\frac{\partial v}{\partial \tau}\right)_p$ is small compared with $3v$, and since it becomes increasingly smaller at higher pressures, we will neglect it. We have seen that at low pressures $\left(\frac{\partial \bar{L}}{\partial p}\right)_\tau$ is positive. But the term $p\left(\frac{\partial v}{\partial p}\right)_\tau$ is negative, so that there is here the possibility of a reversal of sign of $\left(\frac{\partial \bar{L}}{\partial p}\right)_\tau$ at sufficiently high pressures. Now this is an exceedingly unlikely state of affairs, because it would mean that at low pressures the atoms shrink with increasing pressure, but that at sufficiently high pressures they begin to expand again. Hence if we assume that at the utmost $\left(\frac{\partial \bar{L}}{\partial p}\right)_\tau$ can only become zero, we find that the upper limit of $p\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau$ is 3/4 (numerically). If this constitutes any real restriction, the place to look for it is in the compressible substances. Of the metals above, potassium is the most compressible. At 12000 kg., the maximum pressure of these experiments, $p\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau$ has the value 0.19, and thus is still safely below the upper limit. However, if we plot $p\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau$ against p, we obtain approximately a straight line, so that at some pressure below 50,000 kg. there must be an essential change in the character of the relation between pressure and volume. In this connection the possibility of a new polymorphic modification of potassium at high pressures must be kept in mind; it is natural to expect one in analogy with the new form of caesium which I have recently found. A new polymorphic form of potassium at very high pressures also seemed indicated to me a number of years ago [23] by the character of the curve giving change of volume on melting against pressure.

The extreme value of $p\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau$ for potassium is somewhat higher than the value for the most compressible of the organic liquids investigated at high pressures, ether, which has the value 0.17 at 12000 kg.

Change of Compressibility with Pressure. The theory of Born as extended above gives the compressibility as a function of pressure (or

change of volume). Neglecting at first the Schottky effect, or putting $\beta = 0$, we have

$$\chi = -\frac{9\delta_0^4}{a(n-1)}\left[1 + \frac{10+n}{3}\frac{\Delta V}{V_0}\right].$$

It is most interesting to notice that the lattice constants are not contained explicitly in the term giving the variation of compressibility with change of volume, but only the exponent n.

If we had defined the compressibility as $\frac{1}{\delta^3}\frac{d\delta^3}{dp}$ instead of as we did above, then the factor of $\frac{\Delta V}{V_0}$ would have become $\frac{7+n}{3}$. This agrees with a formula which Born has been so kind as to communicate to me in a personal letter.

At high pressures $\frac{\Delta V}{V_0}$ is negative, so that the formula predicts a numerical decrease of compressibility at high pressures, as is most natural. Furthermore, the compressibility decreases more rapidly than the volume itself, and by a factor of the order of a small integer. Now this factor has already been tabulated in Table IV in the column under $2b/a^2$. We see that this quantity is indeed of the predicted order of magnitude, so that Born's theory is suggestive also with regard to the pressure change of compressibility, as well as its absolute magnitude. But the exact value cannot be given by his expression, which demands values of n ranging from negative numbers for Ca and Sr to positive values as high as 95 for W. It is not surprising that the theory does not give precise results here. If we had to object to the single differentiation of the first term of a power series involved in computing the compressibility, still more must we object to the double differentiation involved in the computation of the change of compressibility with pressure.

It is difficult to know exactly how much significance should be attached to the prediction of a correct order of magnitude for the change of compressibility with pressure. Grüneisen's theory of the solid state, which rested on a physically very different picture from Born's, also gave the right order of magnitude.

It is perhaps interesting to consider whether the Schottky term gives plausible results here. If we assume as given by experiment both the compressibility and its variation with pressure, then we have two equations from which we may find both n and β.

We may write the factor of $\frac{\Delta V}{V_0}$ in the form

$$\tfrac{1}{3}\left[8 + 2n + \frac{a(n-1)(n-2)}{a\,\delta_0^4}\chi\right].$$

Now apply this again to calcium. We have the two equations:

$$\frac{9\delta_0^4}{(n-1)\left(a - \frac{\beta}{\delta_0^{n-2}}\right)} = 5.7 \times 10^{-12}$$

$$\tfrac{1}{3}\left[8 + 2n + \frac{a(n-1)(n-2)}{a\,\delta_0^4}\chi\right] = 2.9,$$

with the numerical values of a, δ_0, and χ already used. We notice that β does not enter the second of the two equations above, which is a quadratic in n. Solving this for n, we find

$$n = 7.34.$$

Now for β we have the equation

$$\beta = \delta_0^{n-2}\left[a + \frac{9\delta_0^4}{\chi(n-1)}\right].$$

Substituting numerical values, we find

$$\beta = 2.03 \times 10^{-56}.$$

The result found for n does not appear unreasonable, but the value for β appears to be of the wrong order of magnitude. It would seem, therefore, that the assumption of an inverse ninth power is so poor an approximation when computation involving two differentiations is involved that the inclusion of the Schottky term (which there is every reason to believe actually exists) cannot help matters.

It is to be noticed that if conversely we regard as sufficiently approximate the formula above for the initial compressibility with the Schottky term included, the value of n is very closely determined, if we know merely the order of magnitude of β, by the requirement that β/δ_0^{n-2} be of the same order as "a."

If instead now of assuming a specific form for the repulsive potential, we substitute an arbitrary function, a certain amount of information

as to its behavior can be found in terms of the density, the compressibility, and the change of compressibility with pressure. Let us put in general:

$$\Phi(\delta) = -\frac{a}{\delta} + f(\delta).$$

As before, the general condition of equilibrium is $\Phi + p\,\delta^3$ is to be a minimum with respect to changes of δ. This condition gives:

$$p = -\frac{a}{3\delta^4} - \frac{f'}{3\delta^2}.$$

If δ_0 is the value of δ when $p = 0$,

$$a = -\delta_0^2 f'(\delta_0),$$

and if we furthermore write $(\delta/\delta_0)^3 = V/V_0$, we have the equation

$$f'(\delta) = f'(\delta_0)\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 3p\,\delta_0^2\left(\frac{V}{V_0}\right)^{\frac{2}{3}}.$$

Here V and p are measured quantities, so that if $f'(\delta_0)$ can be found, we have here the means of getting $f'(\delta)$ at any volume (or δ), and hence $f(\delta)$ itself, except for the constant of integration. The most information would be given by the most compressible metals. It is unfortunate that sodium and potassium, the most compressible of the metals above, do not crystallize face centered cubic, so that it is not easy to guess what the complete crystal structure of ions and electrons is, and hence not possible to compute the "a" or the $f'(\delta_0)$.

For less compressible metals, another way of treating the above general equation gives more information. For these metals, the compressibility is given with the accuracy of the experiment by a linear function of the pressure,

$$\chi = \chi_0(1 + \alpha p)$$

where α is an experimental constant, and is negative for all the metals studied above. Now the above equation for Φ can be treated in the general case exactly as we did in the special cases above. Writing again

$$\chi = \frac{1}{\delta_0^3}\frac{d\delta^3}{dp},$$

we may get χ by differentiating the equation of equilibrium, and keeping only small quantities of the first order, we may express χ as a

function of p. It is not worth while reproducing here the algebraic details, but it will be readily found that

$$\chi = \frac{9\delta_0}{\frac{10a}{3\delta_0^3} - f''(\delta_0)}\left[1 + \left\{\frac{14}{9}\chi_0 + \chi_0^2\left(\frac{10a}{27\delta_0^4} + \frac{f'''(\delta_0)}{27\delta_0}\right)\right\}p\right].$$

This formula may be checked in special cases by substituting the particular values of f used above.

In this expression for χ, the term outside the square bracket is χ_0. The factor of p inside the bracket is the empirical constant α. A third relation is given by the stability relations under zero pressure. These three relations may be solved for the three derivatives of giving

$$\begin{cases} f'(\delta_0) = -\dfrac{a}{\delta_0^2} \\ f''(\delta_0) = -\dfrac{9\delta_0}{\chi_0} + \dfrac{10a}{3\delta_0^3} \\ f'''(\delta_0) = \left(-\dfrac{10a}{\delta_0^3} - 42\dfrac{\delta_0}{\chi_0} + 27\dfrac{\alpha\delta_0}{\chi_0^2}\right)\dfrac{1}{\delta_0}. \end{cases}$$

I am much indebted to Mr. J. C. Slater for pointing out to me an error in the original form of my formula for the third derivative.

These formulas may now be applied to numerical computation for those metals above which crystallize face-centered cubic, for in these cases we know the probable complete crystal structure, and can compute the "a." Given the structure, the only additional information needed to compute "a" is the magnitude of the charge on the ion. I have assumed that this charge is three electrons for Al, two for Ca, Fe, Co, Ni, Pd, and Pt, and one for Cu, Ag, Au, Ce, and Pb. With these assumptions the results tabulated in Table VI may be found.

In the first place we notice that the sign of any given derivative is the same for all metals, and that the signs are alternately negative and positive for the first, second, and third derivatives. This is the general character to be expected for a force increasing more and more rapidly as we approach the center of the atom (in particular, a potential as $1/\delta^n$ gives this relative arrangement of the derivatives).

In general the derivatives are numerically larger for the more in-

TABLE VI.

THE FIRST THREE DERIVATIVES OF THE REPULSIVE POTENTIAL.

Metal	$-f'(\delta_0)$	$f''(\delta_0)$	$-f'''(\delta_0)$
Al	17.3×10^{-3}	1.70×10^{6}	$.78 \times 10^{14}$
Ca	4.1	.33	.11
Fe	9.7	1.44	4.9
Co	10.0	1.52	6.6
Ni	10.1	1.54	7.1
Pd	8.1	1.34	7.0
Pt	8.2	1.65	19.2
Cu	2.4	.68	3.4
Ag	1.9	.52	2.1
Au	1.9	.78	7.8
Ce	1.2	.21	.12
Pb	1.3	.27	.55

compressible metals. This is what we would expect, the atoms of the less compressible metals being less deformable.

The order of magnitude of these derivatives now gives a little further information. We would expect that if f is one of the more ordinary mathematical functions the natural sphere of variability of f would have the radius δ, so that the proportional change of f and its various derivatives in a distance δ would be of the order of small numbers. This is true for the first derivative, as we see from the table, for $\delta_0 f''(\delta_0)/f'(\delta_0)$ is of the order of a small number. We can, if we like, reverse this principle, and get the order of magnitude of the unknown f by putting $\delta_0 f'(\delta_0)/f(\delta_0)$ equal to a small number. We shall find $f(\delta_0)$ of the order of 10^{-10}. This is what we would expect on other grounds, for it is also the order of a/δ_0. The same is true of the second derivative, for $\delta_0 f'''(\delta_0)/f''(\delta_0)$ is also of the order of a small number.

The fact that $f'(\delta_0)$, which measures roughly the force of repulsion between adjacent atoms, changes only a few fold in the range of δ_0, has an important bearing on our picture of the nature of the atomic boundaries. The meaning is that the atoms do not behave, when pushed into contact, as if they had rigid boundaries, like two bricks, for example. If this were the case, the relative increase of $f'(\delta_0)$ would be very much more rapid. In my previous work on polymorphic changes under pressure,[24] I found it useful to think of the atoms as more or

less rigid bodies with definite shapes. We now see that this point of view is of restricted usefulness, and in particular is not suited to account for the behavior of the compressibility.

We have up to the present followed Born in entirely disregarding the effect of temperature. This may now be taken into consideration in the following way in the domain in which the temperature is high enough for the classical dynamics to apply, so that we may ascribe to each atom a kinetic energy equal to (3/2) kt. The condition of equilibrium may be conveniently expressed in terms of the "total heat" per unit cell of the lattice, and we will restrict the discussion to substances for which the complete lattice structure of both ions and electrons is like NaCl. For the total heat, H, we have in general the expression $H = E + pV$. Here V is to be taken as the volume of the cell of the lattice or δ^3. E, the energy of the cell of the lattice, is made up of two parts, a potential part, which we write as before as $-\frac{a}{\delta} + f(\delta)$, plus the kinetic part, due to temperature agitation, which is 6kt., since there are in the cell 4 atoms, each with energy (3/2)kt. (we suppose that the kinetic energy of the electrons may be disregarded). Hence

$$E = -\frac{a}{\delta} + f(\delta) + 6\,\mathrm{kt}.$$

The equilibrium condition is that the total heat is constant for changes at constant entropy, and constant pressure. Hence we have

$$d\,(E + p\,\delta^3) = 0$$

where we are to change δ at constant pressure and entropy. This gives

$$\frac{a}{\delta^2} + f'(\delta) + 6\kappa\left(\frac{\partial\tau}{\partial\delta}\right)_s + 3p\delta^2 = 0.$$

To evaluate $\left(\frac{\partial\tau}{\partial\delta}\right)_s$ it is convenient to make connection with the ordinary formulas of thermodynamics for $\left(\frac{\partial\tau}{\partial v}\right)_s$, where v is the volume of material which under standard conditions occupies 1 c.c. We have

$$\left(\frac{\partial\tau}{\partial\delta}\right)_s = \left(\frac{\partial\tau}{\partial v}\right)_s \cdot \left(\frac{\partial v}{\partial\delta}\right)_s.$$

Now $$v = N\delta^3$$

$$\left(\frac{\partial v}{\partial \delta}\right)_s = \frac{dv}{d\delta} = 3N\delta^2, \quad \text{and}$$

$$\left(\frac{d\tau}{\partial v}\right)_s = \frac{\tau\left(\frac{\partial v}{\partial \tau}\right)_p}{C_p\left(\frac{\partial v}{\partial p}\right)_\tau + \tau\left(\frac{\partial v}{\partial \tau}\right)_p^2}.$$

Hence substituting back, we have

$$f'(\delta) = -\frac{a}{\delta^2} - 3\delta^2\left[p + \frac{6\kappa N\tau\left(\frac{\partial v}{\partial \tau_p}\right)}{C_p\left(\frac{\partial v}{\partial p}\right)_\tau + \tau\left(\frac{\partial v}{\partial \tau}\right)_p^2}\right].$$

At zero pressure

$$f'(\delta_0) = -\frac{a}{\delta_0^2} - \frac{\frac{18\kappa\tau}{\delta_0}\left(\frac{\partial v}{\partial \tau}\right)_p}{C_p\left(\frac{\partial v}{\partial p}\right)_\tau + \tau\left(\frac{\partial v}{\partial \tau}\right)_p^2}$$

We have to compare this with the value $f'(\delta_0) = -\frac{a}{\delta_0^2}$, which we previously found, neglecting the temperature effect. For the case of copper, I have substituted numerical values into the second member of the right hand side of the last equation, obtaining 4×10^{-5}, compared with the value 2.4×10^{-3} for a/δ_0^2. Hence the effect of the temperature term is not important.

It is also probable that the new term will not greatly affect the values that we have found for $f''(\delta_0)$ and $f'''(\delta_0)$, or alter the conclusions that we have drawn from these numerical values, because in the case of copper, the numerical value of the new term which stands besides p in the next to the last equation above is 1×10^{10}, and is nearly constant, whereas p varies through a range of 1.2×10^{10}.

SUMMARY.

A new method has been developed by which the linear compressibility of metals or other solid substances with small compressibility may be measured to high pressures. The method is accurate enough to give change of compressibility with pressure and temperature. This paper contains the results of measurements by this method on 30 metals over a pressure range of 12000 kg/cm², and at 30° and 75°. The majority of these metals crystallize in the cubic system, or else in the hexagonal close packed arrangement of spheres, and for them the change of volume may be obtained immediately from the change of linear dimensions, because the compressibility is the same in all directions. Formulas are given for the change of volume as a function of pressure and temperature over the range of the measurements. In general the compressibility decreases with increasing pressure and increases with increasing temperature. The order of magnitude of the change of compressibility or thermal expansion with pressure is the same for all metals. The compressibility changes under pressure by a fraction which is a small number (varying from 2 to 30) times the proportional change of volume under the same pressure, and similarly the proportional change of thermal expansion under pressure is of the order of a small number times the corresponding proportional change of volume.

Six of the thirty substances do not crystallize cubic or in the hexagonal close packed arrangement of spheres, and for these it was established that there are large differences of compressibility in different directions; for one substance, tellurium, it was found that in one direction the linear compressibility is even negative.

In the theoretical discussion it was shown that it is very probable that the forces resisting compression in a metal are the same in nature as those in a salt of the type of NaCl, that is, the metal may be regarded as a lattice of ions and electrons acting on each other by electrostatic forces due to one or more single elementary charges. In addition there is a force of repulsion. Criticism is made of the details of Born's proof of the inverse ninth power law for the potential of the repulsion, and the conclusion drawn that we have not at present a detailed enough knowledge of the structure of the atom to determine the law of repulsion so accurately as to allow us to differentiate the formulas once and twice, as is necessary in computing the compressi-

bility and its change with pressure. It is shown by numerical calculation that the effect discussed by Schottky due to the deformation of the atoms under pressure is of such an order of magnitude that it must be taken into account.

Finally, if we do not assume the specific form of the repulsive potential, but replace it by an arbitrary function, it is shown that the first, second and third derivatives may be computed numerically from experimental data now available for a number of the metals of this investigation. From these numerical values the conclusion is drawn that the boundaries of the atoms cannot be as definite as appeared not unlikely from a study of polymorphic changes under pressure.

I am indebted to my assistant, Mr. I. M. Kerney, for help in making the greater number of the readings.

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25 On reading the galley proofs Professor Richards has been kind enough to call my attention to his estimates of the decrease of compressibility with pressure of the alkali metals on page 24 of Publication No. 76 of the Carnegie Institute of Washington. He finds the average compressibility of sodium between 300 and 500 kg. to be 2/150 less than between 100 and 300, and that of potassium 12/300 less for the same intervals of pressure.